90

TABLE OF COMPOUNDS.

The table below gives the compounds of each metal which are formed in the course of an analysis. It may be followed as a guide in analysis by any one who is familiar with the details involved. It may also be of service to the beginner in gaining a clear conception of the analytical processes.

	$PbCl_2$	$PbCrO_4$							
Gr. I.	Hg_2Cl_2	$(NH_2HgCl + Hg)$							
	$AgCl$	$Ag(NH_3)_2Cl$		$AgCl$					
	HgS	HgS	HgS	$HgCl_2$	Hg_2Cl_2	Hg			
	PbS	PbS	$Pb(NO_3)_2$	$PbSO_4$	$Pb(C_2H_3O_2)_2$	$PbCrO_4$			
	Bi_2S_3	Bi_2S_3	$Bi(NO_3)_3$	$Bi_2(SO_4)_3$	$Bi(OH)_3$	$BiCl_3$	Bi		
	CuS	CuS	$Cu(NO_3)_2$	$CuSO_4$	$Cu(NH_3)_4SO_4$	$CuSO_4$	Cu		
Gr. II.	CdS	CdS	$Cd(NO_3)_2$	$CdSO_4$	$Cd(NH_3)_4SO_4$	$CdSO_4$	$CdSO_4$	CdS	
	As_2S_3	$(NH_4)_3AsS_4$	As_2S_5	As_2S_5 (dslvd. in $(NH_4)_2CO_3$)		As_2S_5	$(NH_4)_3AsO_4$	$MgNH_4AsO_4$	$(As_2S_3 + S)$
	Sb_2S_3	$(NH_4)_3SbS_4$	Sb_2S_5	Sb_2S_5	$SbCl_3$	Sb	$SbCl_3$	Sb_2S_3	
	$SnS;SnS_2$	$(NH_4)_2SnS_3$	SnS_2	SnS_2	$SnCl_4$	$SnCl_2$ (Hg_2Cl_2)			
	$Al(OH)_3$	$AlCl_3$	$NaAlO_2$	$Al(NO_3)_3$	$Al(OH)_3$				
	$Cr(OH)_3$	$CrCl_3$	Na_2CrO_4	$Na_2Cr_2O_7$	Na_2CrO_4	$Na_2Cr_2O_7$	$BaCrO_4$		
	ZnS	$ZnCl_2$	Na_2ZnO_2	$Zn(NO_3)_2$	$[Zn(NH_3)_4](NO_3)_2$	$Zn(C_2H_3O_2)_2$	$Zn(C_2H_3O_2)_2$	ZnS	
Gr. III.	MnS	$MnCl_2$	$MnO(OH)_2$	$MnO(OH)_2$	$HMnO_4$				
	FeS	$FeCl_2$	$Fe(OH)_3$	$Fe(NO_3)_3$	$Fe(OH)_3$				
	CoS	$CoCl_2$	$Co(OH)_3$	$Co(NO_3)_2$	$Co(NH_3)_6(NO_3)_2$	$Co(NO_3)_2$	$(NH_4)_2Co(SCN)_4$		
	NiS	$NiCl_2$	$Ni(OH)_{2-3}$	$Ni(NO_3)_2$	$Ni(NH_3)_6(NO_3)_2$	Ni-dimethylglyoxime			
	$BaCO_3$	$Ba(C_2H_3O_2)_2$		$BaCrO_4$					
Gr. IV.	$SrCO_3$	$Sr(C_2H_3O_2)_2$		$Sr(C_2H_3O_2)_2$	$SrCO_3$	$Sr(C_2H_3O_2)_2$	$SrSO_4$		
	$CaCO_3$	$Ca(C_2H_3O_2)_2$		$Ca(C_2H_3O_2)_2$	$CaCO_3$	$Ca(C_2H_3O_2)_2$	$Ca(C_2H_3O_2)_2$	$CaSO_4$	CaC_2O_4
	MgX_2	$MgNH_4PO_4$							
	NH_4X	NH_4NO_3	$N_2O + 2\ H_2O$						
Gr. V.	KX	KNO_3	KNO_3		$KClO_4$				
	NaX	$NaNO_3$	$NaNO_3$		$NaNO_3$	Na_2SiF_6			
	LiX								

SOLUBILITY OF SOME "INSOLUBLE" SALTS IN WATER.

	Cl	Br	I	SCN	F	S	OH	CO_3	SO_4	CrO_4	C_2O_4
Ag	1.53	0.084	0.003	0.13		0.10	27	17	5500	25	35
Pb	9610	8340	613		700	0.86	75	1	43	0.2	1.5
Hg^{I}	0.5	0.04	0.0002								
Hg^{II}			60	696		0.013	51				
Bi						0.18					
Cu^{II}						0.34					
Cd						1.30					
As^{III}						0.52					
Sb^{III}						1.75					
Zn					5.1	6.88	5				6
Mn						6.23	5.5				
Fe^{II}						6.16	7				
Co						3.79					
Ni						3.62					
Ba					1600		37000	23	2.3	3.8	86
Sr					120		7700	11	110	1200	46
Ca					16		1700	13	2000	4000	5.6
Mg					76		15	800			300

The table gives the number of milligrams of the anhydrous salt that are held in solution by 1 liter (*i. e.*, 1,000,000 mg.) of water at 18–20°.

Joseph Stromada
1924

THE ELEMENTS
OF
QUALITATIVE ANALYSIS

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SEVENTH EDITION

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PREFACE TO THE SEVENTH EDITION.

The sixth edition of this manual, revised by Dr. G. McP. Smith, was published in 1911. Since that time several important improvements in analytical procedure have come into use, notably those involving the dimethylglyoxime and perchloric acid reagents. In order to include these improved procedures, as well as to elaborate or clarify certain other processes, it has seemed desirable to revise the whole book, still retaining, however, all the distinctive style and purposes of the other editions.

The most important changes are as follows: The usual hydrochloric acid method for the separation of the cations of the Tin subgroup has been replaced by the ammonium carbonate-aluminium procedure, for the simple reason that the latter has been found to give better results in the hands of the elementary students in the chemical laboratories at the University of Illinois. The difficult and more or less dangerous separation of nickel and cobalt by means of potassium cyanide has been replaced by the use of dimethyglyoxime as a reagent for nickel, and the thiocyanate test (Vogel's reaction) for cobalt. In the alkali group, potassium is precipitated as the perchlorate by perchloric acid, and sodium as the fluosilicate by fluosilicic acid. Flame tests for these ions are retained, but are used in a more or less secondary way. The method for the detection of anions presents two distinct departures from the former procedure: (1) As far as possible, the anions are tested for in the original substance, without removing the "heavy metals"; (2) in the light of the cations found during the metallic ion analysis, solubility relations of the original substance are used to indicate what anions may be present or absent in the original substance.

It has seemed best to depart from the historical convention of referring to the reactions of the anions as the reactions of the acids of which these anions form the characteristic part. It is decidedly a questionable procedure to direct a student working with a neutral or alkaline solution to "test for acids." A similar inaccuracy is that of referring to the cations as the "metals." For such reasons as these, the more modern usage or "cations" and "anions" has been followed in this book.

Thankful acknowledgment should be made to that large group of instructors and assistants in the Chemistry department at the University of Illinois, who have not only contributed many helpful suggestions, but have faithfully tried out in the laboratory the early ideas that have later been developed into the procedures described in this book.

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Urbana, Illinois
March 28, 1923

PREFACE TO THE FIRST EDITION.

Two reasons have led to the writing of this book. One has been the desire to give to my classes a scheme for qualitative analysis in which points where a beginner is liable to make mistakes are especially guarded by careful and explicit directions for procedure. In this respect the book is the result of considerable experience with classes in the laboratory, where especial pains have been taken to discover the reasons for errors on the part of ordinary students. Qualitative analysis is of no value unless it leads to *certain* results, and the beginner needs to have it impressed upon his mind that certainty can only be attained by performing each operation in exactly the right way. In the author's opinion it is better to teach the student the right way at first, rather than to give only an outline and expect him to fill in the details of manipulation for himself. Every one who has had experience in the matter knows, however, that no amount of careful direction in a text-book can supply the place of constant watchfulness on the part of the instructor.

The second reason for the book has been the desire to connect the reactions given by way of a study of the elements before actual analysis more closely with the course of analysis itself. With this end in view, the reactions given for the student to try before taking up the actual analysis are chosen and arranged in each case with reference to their immediate use in the separation and detection of the elements under consideration. As a result, the preliminary reactions given are fewer in number than is usually the case. These reactions are supplemented, however, by the tables given at the close of Part I. For the idea embodied in these tables and, indeed, for most of the matter which they contain I must acknowledge my indebtedness to Biedermann's "Chemiker-Kalender" for 1887.

The plan to be followed in using this book is largely implied in the text. In the first part of the work it is my custom to have the student perform the preliminary experiments with the metals of a group, writing the equations representing the reactions involved and keeping a careful record of his work. A mixture containing all of the metals of the group is then given and he is required to analyze it, keeping in some systematic form a record of each reagent used and of the results obtained. When the analysis is complete he is required to explain his record and give the reason for each operation. Then mixtures containing part of the metals of the group are given. After completing the study of the metals in this way, simple salts containing one metal and one acid are given for analysis and then general mixtures of various kinds.

The author will be very glad of any corrections or suggestions for improvement which may occur to anyone who uses the book.

W. A. N.

QUALITATIVE ANALYSIS

INTRODUCTION.

Under analytical methods are understood all the operations which are made use of in order to detect in, or obtain from, chemical compounds or mixtures of chemical substances the separate parts of which they are composed. The branch of chemistry under which these methods are treated is called analytical chemistry. Analytical chemistry itself is subdivided into two general parts:

(1) QUALITATIVE ANALYSIS.
(2) QUANTITATIVE ANALYSIS.

Qualitative analysis, with which we are here concerned, deals with the qualitative composition of bodies; *i. e.*, with the separation (either free or in the form of characteristic compounds) and identification of the various elements present in them.

In the course of a qualitative analysis it is usually necessary to transform an element into a number of different compounds, successively, either because the compound first formed is so similar to some compound of another element that it cannot be identified with certainty, or because it is necessary to separate the element from others with which it is mixed or combined. The substances of known behavior by means of which such transformations are brought about are called **reagents.**

A qualitative analysis to be successful must prove with *certainty* that the elements sought are present or that they are absent. The latter is in many cases more important than the former. *Furthermore, some idea should be formed as to the relative quantities in which the elements found are present.* Success can only be attained by the exercise of care in all operations and by the most scrupulous cleanliness.

One who attempts to analyze a substance by following mechanically a scheme which is laid down may sometimes succeed in finding the substances which he seeks, but he is sure to fail in many cases. In order to avoid frequent mistakes the analyst must understand thoroughly the object of every operation and the effect of the operation upon every substance present in the mixture with which he is working. For this reason it is best to perform the operations of analytical chemistry, at first, with substances of known composition, studying carefully the effect upon these of the operations which are afterward to be used in the analysis of unknown substances. *It should also be an invariable rule, when in doubt about a test, to apply the same test to some suitable compound of the substance sought, and to compare the two results.*

Furthermore, it should be borne in mind that the substances tested for may be present in the reagents as impurities. In any case where this seems possible the reagent should be directly tested. The neglect of such blank tests with reagents may give rise to serious errors.

Precipitation is more often used than any other means for the separation and detection of substances. In carrying out this operation, the reagent should always be added gradually, with stirring, and only as long as the precipitate continues to form. This can be determined by allowing the precipitate to settle, or by filtering a little of the liquid, and then adding a drop more of the reagent to the clear solution. In many cases it can be determined by simply noting the odor or color of the solution (*e. g.*, in the precipitation of Group II with H_2S, or of barium with $K_2Cr_2O_7$), since the reagent is present in excess if its characteristic properties are shown by the solution. By adding the reagent in this way, *an undue excess is avoided*, and at the same time the precipitation is proved to be complete. The latter result is essential for the success of an analysis.

A precipitate is **washed** for the purpose of removing the liquid which is mechanically held within its mass. Washing may be performed by decantation or by repeatedly pouring water upon the precipitate as it lies on the filter; unless the precipitate is heavy and settles rapidly, washing upon the filter is usually most effective. It is frequently advisable to remove the first filtrate before beginning to wash a precipitate, as the washings sometimes pass through turbid even when the first filtrate is clear. *Too much emphasis cannot be laid upon the fact that the success of an analysis depends very greatly upon complete precipitations, and upon the proper washing of the precipitates.* The object of precipitation is to separate one or more substances from others in solution, and it is obvious that a complete separation is not attained unless the precipitation is complete and the precipitation is entirely freed from the liquid in which it was produced. The analyst should always assure himself that the precipitate is thoroughly washed by testing the last portions of the filtrate. (If the solution contains acid or alkali, for example, the precipitate should be washed as long as the filtrate reacts with litmus paper.)

The precipitate sometimes assumes the **colloidal state** to a certain extent; in this state it is under certain conditions insoluble and under others soluble. The insoluble form is called the **hydrogel,** and the soluble the **hydrosol.** When in the hydrosol condition substances enter the solvent in suspension in the form of minute particles, and, on filtration, these pass through the filter. Some precipitates assume the hydrosol condition when brought in contact with pure water, *e. g.*, when being washed upon the filter. When this happens, the filtrate becomes turbid, and the pores of the filter are apt to become clogged, thus rendering further washing almost impossible. Heat, agitation, or the addition of certain salts or acids will often cause the precipitation of colloidal substances.

IONIZATION IN SOLUTION.

Since in the following we shall have to deal very extensively with reversible ionic reactions, it will not be out of place at this point to review the evidence that the molecules of acids, bases, and salts are dissociated into parts by the aqueous solvent.

All acids, bases, and salts are made up of two radicals, and the reversible double decompositions into which they enter with other acids, bases, and salts consist in exchanges of these radicals. All acids, for example, act as if composed of hydrogen and a negative atom or group, and their sour taste and their effect on litmus seem to be properties of this easily separable hydrogen. Similarly, the peculiar properties of bases seem to be due to the easily separable hydroxyl, which they all contain.

It is, however, chiefly in aqueous solution that the special properties of acids, bases, and salts become apparent. Their behavior is often quite different in the absence of this solvent. If, for example, potassium chlorate and acid sodium tartrate, each in the form of a powder, are gently mixed together, there is no evidence of a chemical change. But if we apply heat to the mixture, a violent interaction takes place, accompanied by the evolution of heat and light. If, on the other hand, the two substances are dissolved in water before being brought in contact, the difference is very great. A white, crystalline precipitate separates, which on examination is found to be cream of tartar, and the liquid contains mainly sodium chlorate in solution. The two actions may be represented by the respective equations:

$$6NaHC_4H_4O_6 + 10KClO_3 \rightarrow 3Na_2CO_3 + 10KCl + 21CO_2 + 15H_2O,$$
$$\text{and } NaHC_4H_4O_6 + KClO_3 \leftrightarrows KHC_4H_4O_6 + NaClO_3.$$

In the interaction between the dry substances the molecules are completely disintegrated, and the change is not reversible. In the action in water no heating is required, and certain atomic groupings, called radicals, are transferred as wholes, in a very quiet manner, from one state of combination to another; and in this case the action is reversible.

Again, as an example of the different behavior of an acid in the practical absence of water, and in its presence, we may cite the evolution by zinc of sulfur dioxide from concentrated sulfuric acid, on heating, and the evolution by the same metal of hydrogen from the dilute acid, with or without the application of heat.

In the cases of acids, bases, and salts in aqueous solution, each compound usually splits in the same way. Thus, potassium chlorate gives double decompositions involving K and ClO_3—it gives no precipitate with silver nitrate, for example, because silver chloride is not produced by the interaction of the two salts, and the silver chlorate which is formed is not insoluble. Similarly, acids always offer hydrogen in exchange, and bases hydroxyl, so that nitric acid behaves as if composed of H and NO_3, and potassium hydroxide as if composed of K and OH. The result is that we can make a list of the atoms and radicals, such as K, Ag, H, OH, Cl, NO_3, ClO_3, etc., exchanged by acids, bases, and salts in their interactions. The molecule of each acid, base, or salt contains at least two such parts.

The question naturally presents itself whether solution in water simply produces in the molecules of these substances a sort of "*plane of cleavage*" and thus leads to a uniform kind of chemical change, or whether it *actually divides* the molecules into separate parts, and leaves subsequent chemical actions to occur by cross-combination of the fragments. The question is not answered by the chemical evidence alone; it can, however, be answered by a study of the physical properties of solutions.

Laws of Freezing-Point Depression.—If a substance such as sugar is dissolved in water, and the resulting solution is sufficiently cooled, a separation of pure ice takes place, and it is found that the temperature at which equilibrium exists between the very small quantity of ice and the solution is lower than the freezing-point of pure water. Furthermore, the lowering of the freezing-point of the solvent is directly proportional to the weight of sugar dissolved in a given amount of the solvent. But if equal weights of different substances, such as sugar, glucose, alcohol, etc., are dissolved in equal portions of the same solvent, different freezing-point depressions are produced. If, however, *equal numbers of* *molecules* of different solutes are dissolved in equal quantities of the same solvent, then the same lowering of the freezing-point is observed in every case. Thus, solutions containing 342 grams of sugar ($C_{12}H_{22}O_{11}$), or 180 grams of glucose ($C_6H_{12}O_6$), or 74 grams of methyl acetate ($CH_3.C_2H_3O_2$) or 46 grams of alcohol (C_2H_5OH)—*i. e.*, 1 gram molecule in each case—in 10,000 grams of water, all show a freezing-point lowering of 0.185°.

It is important to emphasize that the freezing-point lowering depends solely upon the concentration of the solute particles; what these particles themselves may be makes no difference. One-fourth mol each of the four substances dissolved together in 10 liters of water would give the same depression as 1 mol of any one of the substances in the same quantity of water, since in both cases the actual number of particles is the same.[1]

The substances which present the most conspicuous exceptions to the above laws are acids, bases, and salts, in aqueous solution; the freezing-point is generally lower than we should expect from the concentration of the solution. Thus, a solution containing 58.5 grams of sodium chloride in 10 liters of water is found to freeze at –0.350°. If sodium chloride were present only in the form of NaCl molecules in the solution, the freezing-point would be –0.185°, as with the other substances named. That the actual lowering is 0.350°, or $\frac{0.350}{0.185} = 1.89$ times as great as that which would result if sodium chloride behaved in the same manner as sugar, etc., shows that the solution contains a larger number of particles than the number of chemical molecules (NaCl). The explanation would be simple if, for example, out of 100 of the original NaCl molecules, 89 should, when dissolved, dissociate into the smaller particles Na and Cl, while 11 remained united in the chemical molecules NaCl. The total number of particles would then be 1.89 times the number of the original chemical molecules. Likewise, of 100 molecules of such a substance as barium chloride, $BaCl_2$, 75 molecules might dissociate into 75 particles of Ba and 150 of Cl, while there remained 25 of the original $BaCl_2$ molecules, thus giving 250 particles in solution. This supposition is in accord with the actual freezing-point (–0.469°) of a 0.1 molal barium chloride solution, which indicates the presence of $\frac{0.469}{0.185} = 2.5$ times as many particles as the original number of chemical molecules ($BaCl_2$).

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[1] These laws describe the facts very closely when the solutions are dilute. They hold only when there is no chemical interaction between solute and solvent, and when pure ice separates from the freezing solution.

The same conclusion, that the molecules of acids, bases, and salts are dissociated in aqueous solution, follows also from the study of the boiling-points and of the osmotic pressures of solutions.

The Ionic Theory.—It is seen then that a solution of hydrogen chloride, or sodium nitrate, or potassium hydroxide, etc., contains, besides undivided molecules of the solute, at least two other kinds of particles, H, Na, K, Cl, NO_3, OH, etc., which result from the dissociation of the molecules. These subdivisions of the original molecules have distinct physical and chemical properties of their own; the particles of Na and Cl, for example, are apparently as different from free molecular sodium and chlorine as is red phosphorus from yellow, or graphite from diamond. The explanation of the difference between these particles and ordinary molecules is best arrived at through a study of the electrical behavior of such solutions.

If the platinum terminals of a battery are dipped into a vessel filled with pure water, no passage of electricity will take place through the water; and if the same experiment is tried with anhydrous, liquid hydrogen chloride, the latter is also found to be a non-conductor. But if the two liquids are mixed, or if gaseous hydrogen chloride is dissolved in water, and the solution is tested in the same manner, it is found that electricity readily passes through the liquid. At the same time, equivalent quantities of hydrogen and chlorine are separated at the negative and positive pole, respectively. We have already seen that upon solution in water a fraction of the molecules of hydrogen chloride are broken up into peculiar particles of hydrogen and of chlorine; but, even if the hydrogen and chlorine particles were composed of conducting material, distributed throughout the non-conducting solvent as independent particles, they could not furnish a continuous medium for the passage of electricity. This will be clear when we recall the fact that although liquid mercury is an excellent conductor, mercury vapor, composed as it is of conducting particles, is not a conductor. Why then should the hydrogen and chlorine particles be attracted by electrically charged plates lowered into the solution?

The answer to this question is obvious. The only bodies which are found to be conspicuously attracted by electrically charged objects are bodies which are already provided with electric charges of their own. We are thus led to assume that molecules which undergo dissociation in solution divide themselves into a special kind of electrically charged sub-molecules. Since the solution itself has no charge, equal quantities of positive and negative electricity must be produced. Moreover, since like kinds of electricity repel one another, while unlike kinds attract each other, and since hydrogen and the metals are separated at the negative pole, while chlorine and other similar radicals go to the positive pole, we conclude that, upon solution in water, hydrogen chloride undergoes the change represented by the equation:

$$HCl \rightleftarrows H^{+} + Cl^{-}.$$

In a similar manner, in aqueous solution,

$$AgNO_3 \rightleftarrows Ag^{+} + NO_3\ ,$$
$$NaOH \rightleftarrows Na^{+} + OH^{-},$$
$$K_2SO_4 \rightleftarrows 2K^{+} + SO_4^{--}.$$

The negatively charged plate attracts all the positively charged particles, and although these particles are in continuous and irregular motion, they nevertheless begin to move toward the plate in question; their motion in this direction is further encouraged by the fact that they are at the same time repelled by the positively charged plate. For similar reasons, the negatively charged particles travel in the opposite direction. Upon coming in contact with the plates, the particles lose their electric charges and change into the ordinary free forms of matter of which they are composed.

If these are hydrogen and chlorine, the atoms of each unite in pairs to form molecules of ordinary gaseous hydrogen and chlorine. If however the particles are sodium and CO_3, for example, we find that equivalent amounts of hydrogen and oxygen are evolved at the cathode and anode, respectively; but if, instead of being made of platinum, the cathode consists of mercury, and the anode of silver, then the discharged sodium particles are taken up by the mercury, with which they form $NaHg_5$, and the $CO_3{=}$ particles by the silver, with which they form insoluble Ag_2CO_3.

By rapidly whirling a tube filled with a solution of hydrogen, lithium, sodium, or potassium iodide in a powerful centrifugal machine it has been shown that the solution at the peripheral end of the tube acquires a negative electrical charge, while that at the central end acquires a positive charge. This behavior is readily explained by the ionic theory: The heavy iodide ions are driven outward by the centrifugal force so that they are present in excess at the outer end of the tube, while the lighter positive ions are left in excess in the central end. Upon ceasing to rotate the tube, the distribution of the positive and negative ions in the solution instantly reassumes its original condition.

Nomenclature.—The electrically charged radicals which result from the dissociation of the molecules of acids, bases, and salts upon solution in water, are called *ions*. The dissociation of molecules into ions is called *ionization*, and substances which are *ionized* are called *ionogens*. The positive ions, which separate at the negative pole, are called *cations* and the negative ions are called *anions*. Upon the ions from one molecule, the number of positive and negative charges is always equal; the number of charges upon any ion is the same as its valence as a radical.

Degree of Ionization.—In solutions made from salts, the greater, and by far the most active, part of the contents is almost invariably ionic. In the case of acids and bases there is a wider range, and a larger proportion of these are less highly ionized; but even then the ions are nearly always much more active than the undissociated molecules. The acids and bases that are commonly called "*strong*" are highly ionized, *i. e.*, their solutions are especially active because they contain high H^+ and OH^- ion concentrations. The degree of ionization of the commoner ionogens in normal and 0.1 normal solution is given in the following table:

1. ACIDS.

	Per cent. ionized.	
	Normal.	0.1 Normal.
H^+Cl^-, H^+Br^-, H^+I^-,	78.4	90
$H^+NO_3^-$,	82.0	90
$H^+HSO_4^-$,	51.0	60
$H^+HC_2O_4^-$,	....	34
$H^+C_2H_3O_2^-$,	0.4	1.3
$H^+HCO_3^-$,	....	0.12
H^+HS^-	....	0.05
H^+CN^-	....	0.01

2. BASES.

K^+OH^-	77	86
Na^+OH^-	73	86
$NH_4^+OH^-$[1]	0.4	1.5

3. SALTS.[2]

Type M^+A^-(*e. g.*, $AgNO_3$, KCl, etc.),	75	86
Type $M^{++}A_2^-$ (*e. g.*, $Ba(NO_3)_2$, $SrCl_2$, etc.),	53	72
Type $M_2^+A^{--}$ (*e. g.*, K_2SO_4, etc.),	53	72
Type $M^{++}A^{--}$ (*e. g.*, $MgSO_4$, etc.),	....	45

THE LAW OF MASS-ACTION.

Ionic Equilibrium.—When acetic acid is dissolved in water, it ionizes as follows:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-.$$

---

[1] NH_4OH also dissociates into $NH_3 + H_2O$, and the apparently very low ionization is partly due to this.

[2] Notable exceptions are $CdCl_2$ and $HgCl_2$, which in 0.1 N solution are 47% and 0.01% ionized, respectively, and $Pb(C_2H_3O_2)_2$, which gives a very low concentration of Pb^{++} ions.

The quantity of the molecular acid that is ionized per second in a given quantity of the solution is proportional to the concentration of the un-ionized molecules (C_1), while the amount of the ions that unite to form molecules depends upon the frequency of the encounters of the two kinds of ions, which in turn is proportional to the product of their concentrations ($C_2 \times C_3$).

The speed of the respective actions will therefore be

$$S_1 = C_1 \times F_1 \text{ and } S_2 = C_2 \times C_3 \times F_2,$$

where F_1 is the intrinsic tendency of $HC_2H_3O_2$ to ionize, and F_2 is that of H^+ and $C_2H_3O_2^-$ to combine.

When equal amounts of material are being transformed each way, *i.e.*, at equilibrium, we have $S_1 = S_2$, whence

$$C_1 \times F_1 = C_2 \times C_3 \times F_2,$$

or

$$\frac{C_2 \times C_3}{C_1} = \frac{F_1}{F_2} = K \tag{1.}$$

$\frac{F_1}{F_2}$, being the ratio of two constants, is constant (= K). This ratio of the affinities driving the opposed actions is called the *affinity constant* of the reversible reaction. At any given temperature, the numerical value of K remains the same no matter what the total concentration of the solution may be. For example, the data, obtained from conductivity determinations, in regard to acetic acid, at 18°, are as follows:

Total molal concentration of acid.	Proportion ionized.	Molal concentration of H^+, (C_2); and of $C_2H_3O_2^-$, (C_3).	Molal concentration of $HC_2H_3O_2$, (C_1).
1.	0.0041	0.0041	1. —0.0041
0.1	0.0130	0.0013	0.1 —0.0013
0.01	0.0407	0.000407	0.01—0.000407

Substituting these data in equation (1) (page 11), we get:

$$\frac{(0.0041)^2}{0.9959} = 0.0000169; \quad \frac{(0.0013)^2}{0.0987} = 0.0000171;$$

$$\text{and } \frac{(0.000407)^2}{0.009593} = 0.0000172.$$

It is seen that, although the third solution is a hundred times more dilute than the first, and the degree of ionization has increased ten times, the values of **K** are practically identical in both cases.[1]

The Common-ion Effect.—When, through the presence of two substances with a common ion, C_2 is not equal to C_3, the law of mass action (formula 1) still holds. For example, if a single liter of solution contains 1 mol each of acetic acid and sodium acetate, the solution is uni-molal in respect to the acid and to the salt as well, and all the $C_2H_3O_2^-$ ions are available for uniting with either H^+ or Na^+ ions. C_3 in formula (1) is, therefore, abnormally large, and the ionization of the acid is repressed. In uni-molal sodium acetate, 0.53 of the salt is ionized, and, initially in the mixture of acid and salt, C_3 will be $0.53 + 0.004 = 0.534$, or nearly 134 times as large as in the acid alone. Since the fraction $\frac{C_2 \times C_3}{C_1}$ remains constant, and since C_1 is not appreciably increased by the small additional amount of molecular acid formed, the product $C_2 \times C_3$ must recover a value much nearer the old one; *i. e.*, C_2 must be diminished to about 1/134 of its former magnitude. The ionization of the salt is, of course, reduced also, but the $C_2H_3O_2^-$ ions furnished by the acid are relatively so few (0.004: 0.53) that their effect upon the ionization of the salt is imperceptible. The H^+ and $C_2H_3O_2^-$ ions disappear in equivalent quantities, for they unite; but there are so few of the former that practically none of them remain, while *there are so many of the latter that the loss of a very few is not noticed.*

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[1] When data like the above are applied in this way to the cases of highly ionized substances, the values of **K** are far from constant. The cause of this is not yet known. However, the general conclusions arrived at through the application of such data are as a rule not invalidated by this fact.

The student should especially note that the concentration of a given ion can be lowered in this way to almost nothing *only when that ion unites with an ion added to form a very slightly ionized substance, such as acetic acid, ammonium hydroxide, etc.* The addition of sodium chloride to sodium hydroxide solution, for example, produces no very marked effect, but the addition of ammonium chloride to an ammonium hydroxide solution greatly reduces the hydroxide ion concentration; similarly, the addition of sodium acetate to a hydrochloric acid solution greatly lowers the hydrogen ion concentration, owing to the formation of the slightly ionized acetic acid.

The Theory of Precipitation.—One of the commonest and most interesting applications of the above conceptions is met with in connection with saturated solutions, especially those of relatively insoluble substances.

When a substance, like salt or sugar, is placed in contact with a liquid, such as water, there is a tendency for molecules to leave the solid and enter the liquid; after having done this the molecules move in every direction, and consequently some of them return to the solid and attach themselves to it. This occurs the more frequently, the greater the concentration of the molecules in the liquid becomes, until, finally, a stage is reached at which the number of molecules leaving the solid has become the same as the number of those deposited upon it in a given time. If the entire liquid is equally charged with dissolved molecules, the liquid immediately surrounding the solid will lose none by diffusion, and a condition of equilibrium will have been established. The quantity of undissolved solute remains thereafter unchanged, no matter how long the materials are left in contact. It is at this point that the solution is said to be saturated with respect to the substance dissolving.

In the case of silver bromate, for example, we have the following scheme of equilibria:

$$AgBrO_3(\text{solid}) \rightleftarrows AgBrO_3(\text{dissolved}) \rightleftarrows Ag^+ \; BrO_3^-.$$

The solid $AgBrO_3$ molecules tend to enter the solution, while at the same time dissolved $AgBrO_3$ molecules tend to come out of solution, and the solution is saturated when these tendencies produce equal effects. The ions and any foreign material present do not deposit themselves upon the solid; they take, therefore, no *direct* part in the equilibrium which controls solubility. That is, *in solutions saturated at a given temperature by a given solute, the concentration of the dissolved molecules considered by themselves will be constant no matter what other substances may be present, provided their quantity is not great enough to change the nature of the solvent.*

The total solubility of an ionogen, as we ordinarily use the term, is made up of a molecular and an ionic part. The latter is not constant when a foreign substance giving a common ion is already in the liquid. In a saturated solution of silver bromate, for example we have the mathematical relation (formula 1):

$$\frac{[Ag^+] \times [BrO_3^-]}{[AgBrO_3]} = \mathbf{K}, \text{ or } [Ag^+] \times [BrO_3^-] = \mathbf{K} \times [AgBrO_3]$$

But since, in a saturated solution, the concentration of the molecular salt $[AgBrO_3]$ is constant, its product into **K** is also constant. That is, *in a saturated solution of a given ionogen the product of the molal concentrations of the ions* (*e. g.*, $[Ag^+] \times [BrO_3^-]$) *is constant.* This product is called the **solubility product,** because the two values jointly determine the magnitude of the total solubility of the ionogen. The solubility of the molecules cannot be diminished, but the ionic part of the solute may become vanishingly small if the concentration of the common ion is made relatively great as compared with that of the other ion of the solute.

The theory of the precipitation and solution of *slightly soluble* ionogens may be summed up as follows:[1]

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[1] That is, of ionogens formed by the union of one cation and one anion only. In other cases the solubility product should contain ion-concentrations raised to the second, third, etc., powers; but in reality the relations are not so simple. Thus, in the case of $PbCl_2$, if a soluble salt giving chloride ions (*e. g.*, NaCl) is added to the saturated solution, some $PbCl_2$ will be precipitated in accordance with the theory; but the addition of a salt giving the common bivalent ion (*e. g.*, $Pb(NO_3)_2$), for some reason not yet known, fails to produce a precipitate.

If the product of the molal concentrations of any pair of ions in a solution becomes greater than the solubility product for the saturated solution of the ionogen formed by their union, the latter will be precipitated until the ion-concentration product has been reduced to the value of the solubility product. And conversely, *if the product of the concentrations of any pair of ions in a solution is less than the solubility product for the saturated solution of the ionogen formed by their union, the latter, if present in sufficient excess, will continue to dissolve until the ion-concentration product has been increased to the value of the solubility product.*

As an illustration of the effect of adding a salt with a common ion to the saturated solution of another salt, the following table is offered:

COMMON ION EFFECT ON THE SOLUBILITY OF $AgBrO_3$.

Mols of $AgNO_3$ per liter.	Mols of $KBrO_3$ per liter.	Solubility of $AgBrO_3$ in Mols.	Calculated.
0	0	0.00810	....
0.0085	0	0.00510	0.00504
0	0.0085	0.00519	0.00504
0.0346	0	0.00216	0.00206
0	0.0346	0.00227	0.00206

It is seen that a small excess of either salt reduces the solubility to one-fourth the value for pure water.

PART I.

A. DETECTION OF THE METALLIC IONS.

GROUPS OF THE METALS.

For the purpose of qualitative analysis the metallic ions are divided into five groups in accordance with their deportment toward various reagents.

Group I.—Metals whose chlorides are insoluble in water and dilute acids: **Lead** (chloride slightly soluble), **silver, mercurous mercury.**

Group II.—Metals whose chlorides are soluble, but whose sulfides are precipitated from dilute acid solutions: **Mercuric mercury, lead, bismuth, copper, cadmium, arsenic, antimony, tin.**

Group III.—Metals whose sulfides are not precipitated from dilute acid solutions, but whose hydroxides or sulfides are precipitated by ammonia and ammonium sulfide, in the presence of ammonium salts: **Aluminium, chromium, zinc, manganese, iron, cobalt, nickel.**

Group IV.—Metals whose hydroxides and sulfides are soluble in the presence of ammonium salts, but whose carbonates are precipitated in the presence of ammonium salts: **Barium, strontium, calcium.**

Group V.—Metals whose chlorides, hydroxides, sulfides and carbonates are soluble in the presence of ammonium salts: **Magnesium, potassium, sodium, ammonium.**

GROUP I.

HYDROCHLORIC ACID GROUP.

To this group belong **lead, silver, and mercury in mercurous salts.** It is often called the silver group.

The chlorides of the metals of this group are insoluble in water and dil. HCl, with the exception of lead chloride, which is very sparingly soluble. If present in sufficiently small amount, lead may not be found at all in the first group; it should, however, if present, always be detected and removed in Group II, whether it was found in Group I or not.

From an alkaline solution HCl may also precipitate many other substances; *e. g.*, As_2S_5 from an ammonium sulfide solution, metallic hydroxides from solution in caustic alkalies, etc. *If, therefore, the original solution is alkaline, do not add HCl, but see Part II.*

The sulfides of the metals of this group, like those of mercuric mercury, bismuth, copper and cadmium, are insoluble in cold, dilute acids and in ammonium sulfide.

PRELIMINARY EXPERIMENTS.

In performing the experiments with each metal the student should keep a concise record of his work,[1] and afterward in analyzing a solution containing the metals of the group, he should refer to his record and *be sure that he understands thoroughly the effect of every reagent which he uses, and the object of every operation which he performs.*

Lead.—Take 2 cc. of a solution of a lead salt (*e. g.*, the nitrate) in a test-tube, add a little dil. HCl, shake vigorously and allow the white precipitate of $PbCl_2$ to settle. Decant the liquid. Boil the precipitate with water, pour off the solution, boil again with water and repeat until the lead chloride is completely dissolved. Test different portions of the solution with H_2S, dil. H_2SO_4 and $K_2Cr_2O_7$ solution. The precipitates are PbS, $PbSO_4$ and $PbCrO_4$.

Silver.—Take 2 cc. of a solution containing silver. Add dilute HCl, with shaking, as long as white, curdy AgCl continues to form. Allow the AgCl to settle, decant, boil the precipitate with water, decant through a filter and test the filtrate for Ag^+ with H_2S. Add to the AgCl remaining in the test-tube NH_4OH and shake. To the solution, which contains the silver as ammonio-silver chloride, $[Ag(NH_3)_2]Cl$, add dil. HNO_3. The precipitate is AgCl.

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[1] See Appendix, p. 109, for form of record.

AgCl, though very slightly soluble in water, dissolves readily in ammonia, owing to the union of the Ag^+ ions in the saturated solution with NH_3 molecules to form the complex cation $Ag(NH_3)_2^+$. This cation, however, is very slightly dissociated according to the equation: $Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2NH_3$. Upon the addition of HNO_3, OH^- ions in the solution unite with H^+ ions of the acid to form water, and in consequence the entire equilibrium, $NH_3+H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-$, is displaced toward the right; the removal of the NH_3 molecules enables the complex cation to further dissociate, with the result that the AgCl is reprecipitated, since the solubility product for its saturated solution is very soon exceeded.

Mercury in Mercurous Salts.—Take 2 cc. of a solution of mercurous nitrate, $Hg_2(NO_3)_2$, add dil. HCl, shake, decant, boil the Hg_2Cl_2 three times with about 10 cc. of water, decanting each time, to remove mercuric salts, then boil a fourth time, decant through a filter and test the filtrate for Hg_2^{++} with H_2S. Add NH_4OH to the Hg_2Cl_2 remaining in the test-tube. The mercurous chloride is changed to a black mixture of ammonobasic mercuric chloride and mercury, $NH_2HgCl+Hg$.

ANALYSIS.

I. Hydrochloric Acid Group.

(1.) Precipitation.—Add to the neutral or slightly acid solution in a small beaker 4 cc. of dil. HCl (sp. gr. 1.12), and dilute the mixture to 40 cc. The precipitation of Group I is carried out in this way in order that the acid concentration of the filtrate may be suitable for the precipitation of Group II by H_2S. *If the solution is at the start strongly acid with an unknown quantity* of H_2SO_4, *or if it contains free* HNO_3, *dil. HCl may be added here drop by drop as long as a precipitate continues to form and the mixture filtered without previous dilution.* If the dilute solution already contains HCl, Group I is of course absent.

a. *No precipitate is formed.* Silver and mercurous mercury are absent. Pass on to (**5**).

b. *A precipitate may contain* $PbCl_2$, $AgCl$, Hg_2Cl_2. Shake the mixture, allow it to stand 2 or 3 minutes, filter, and wash the precipitate twice with small portions of cold water, rejecting the washings. Treat the filtrate by (**5**.).

(**2**.) **Lead.**—Pour a 5 to 10 cc. portion of boiling water repeatedly over the precipitate on the filter. Divide the filtrate in two portions: to one add dil. H_2SO_4. A white pulverulent precipitate is $PbSO_4$. To the other portion add $K_2Cr_2O_7$ solution. A yellow precipitate is $PbCrO_4$.

(**3**.) **Silver.**—If lead has been found, wash the precipitate with hot water until the wash water no longer gives a precipitate with dil. H_2SO_4. Then pour a few cc. of NH_4OH repeatedly through the filter, and acidify the filtrate with HNO_3. (*In every case like this, test the solution with litmus paper*, **after having thoroughly mixed the liquids.**)

If the $PbCl_2$ is not washed out, it is changed by the NH_4OH to a white basic salt, which runs through the filter and gives a turbid filtrate, but which is soluble in the HNO_3. If much mercury is present and silver is not found here, it is best to test the black mercury residue for silver as follows: Punch a hole in the filter and rinse the residue into a test-tube; allow to settle, and decant the liquid. Boil the solid with a little dilute *aqua regia*,[1] dilute the solution with an equal quantity of water, filter, and if a residue (AgCl) remains test it with NH_4OH and HNO_3.

(**4**.) **Mercurous Mercury.**—If the precipitate on the filter blackens on treatment with NH_4OH, (**3**.), the presence of mercurous mercury is shown.

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[1] *Aqua regia* should always be freshly prepared before use. In this case, cover the solid with 2 or 3 cc. dil. HCl, add 2 or 3 drops conc. HNO_3 and boil.

GROUP II.

HYDROGEN SULFIDE GROUP.

The chlorides of the metals of this group are soluble, but the sulfides are insoluble in cold dilute acids. The group is divided into two subgroups.

A. The Copper Group. To this belong **mercury in mercuric salts, lead, bismuth, copper** and **cadmium.** The sulfides of the metals of this subgroup are insoluble in yellow ammonium sulfide.

B. The Tin Group.—To this belong **arsenic, antimony** and **tin.** The sulfides of the metals of this subgroup are all soluble in yellow ammonium sulfide, with which they give the soluble thio-salts $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$. On adding dil. HCl to the solution the thio-salts are decomposed; H_2S is evolved, and a precipitate of As_2S_5, Sb_2S_5 and SnS_2 is obtained.

A. The Copper Group.

PRELIMINARY EXPERIMENTS.

Mercury in Mercuric Salts.—Take 1 cc. of mercuric chloride, add a few drops of dil. HCl, dilute to 10 cc., pass H_2S slowly as long as a change is observed in the color of the precipitate, warm, allow to settle and wash three or four times by decantation. Add 1 or 2 cc. of dil. HNO_3, boil for a short time; then add 1 or 2 cc. dil. HCl, and boil again. The mercury dissolves as $HgCl_2$. Cool dilute, filter, if necessary, and add a small quantity of $SnCl_2$; at first drop by drop, and then 2 or 3 cc. At first, white Hg_2Cl_2 precipitates; the excess of $SnCl_2$ reduces the white precipitate to gray, finely divided mercury.

Lead.—Take 10 cc. of a solution of $PbCl_2$, add a little HCl, warm, pass H_2S, allow the PbS to settle, decant, wash, boil the precipitate with 1 cc. of dil. HNO_3. To the solution containing

$Pb(NO_3)_2$, add 2 or 3 cc. dil. H_2SO_4 and evaporate almost to dryness in a small Pyrex[1] beaker or evaporating dish. The end point will be indicated by the solution beginning to give off dense white fumes of H_2SO_4. (These fumes may be distinguished from steam and HNO_3 vapors not only by their density, but by their causing involuntary coughing.) Allow to cool thoroughly, and pour into 10 or 15 cc. of cold water in a test tube. Let the precipitate settle, and rinse the beaker with the clear solution so as to transfer all the precipitate to the tube. Decant, leaving the precipitate in the tube. Dissolve the precipitate in 10 cc. of warm 10% $NH_4C_2H_3O_2$ solution, and add a few drops of $K_2Cr_2O_7$ solution and 2 or 3 cc. of $HC_2H_3O_2$. The precipitate is $PbCrO_4$, "chrome yellow." The $PbSO_4$ dissolves in $NH_4C_2H_3O_2$ solution owing to the fact that $Pb(C_2H_3O_2)_2$ furnishes only a very low concentration of Pb^{++} ions.

Bismuth.—Take 2 cc. of a solution of $BiCl_3$. Dilute to 10 cc. This may cause a precipitation of BiOCl. Whether it does or not, warm, pass H_2S, allow the Bi_2S_3 to settle, decant, wash and boil the precipitate with a few cc. of dil. HNO_3. To the solution of $Bi(NO_3)_3$ add 2 or 3 cc. conc. H_2SO_4, and evaporate in a small beaker until dense white fumes of H_2SO_4 begin to come off. Cool, pour into 10 or 15 cc. of cold water in a test-tube, allow any precipitate to settle, and rinse the beaker with the clear solution returning the solution to the test-tube. To the cold solution add NH_4OH until the solution is alkaline to litmus paper. The precipitate is $Bi(OH)_3$. Filter, wash once, and pour through the filter a little freshly prepared Na_2SnO_2 solution.[2] The black residue is metallic bismuth.

Copper.—Take 2 cc. of a copper salt solution, add a few drops of dil. HCl, dilute to 10 cc., warm, pass H_2S, allow the CuS to settle, decant, wash, dissolve in 1 cc. dil. HNO_3 by boiling, add 1 or 2 cc. dil. H_2SO_4 to the nitrate solution and then NH_4OH until its odor persists strongly after shaking. The blue color is due to the complex ion $Cu(NH_3)_4^{++}$ (see under Cadmium). Acidify a portion of the solution with $HC_2H_3O_2$ and add 1 or 2 drops $K_4Fe(CN)_6$ solution. The red precipitate is $Cu_2Fe(CN)_6$. To the remainder of the solution add dil. H_2SO_4 till the deep blue color just disappears, then some iron filings and boil for a short time. Filter, acidify with dil. H_2SO_4, unless the solution is still acid, dilute and pass H_2S into the liquid.

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[1] A small porcelain dish may be used here instead of the Pyrex beaker. As a rule, however, in most analytical procedures, Pyrex glassware is preferable to porcelain not only because there is not the likelihood of breakage upon evaporation to dryness, but more particularly because it is more resistant to corrosion by acids.

[2] Made by adding to 2 or 3 cc. of $SnCl_2$ solution in a test-tube an excess of NaOH solution. A white precipitate of $Sn(OH)_2$ forms first, and later redissolves in the excess NaOH. Be sure that the final solution reacts alkaline to litmus paper. If not, not enough NaOH has been used.

Cadmium.—To 5 cc. of a cadmium salt solution add 4 cc. HCl (sp. gr. 1.12), and dilute to 40 cc. Heat the solution nearly to boiling, and pass H_2S into the hot liquid for 2 or 3 minutes. Does a precipitate form? If so, filter. Now cool the filtrate, add to it 60 cc. water, and saturate the resulting solution in the cold with H_2S. Filter, wash the precipitate, and boil it in a test-tube with 2 or 3 cc. dil. HNO_3. Add to the solution 1 or 2 cc. dil. H_2SO_4, and then NH_4OH until its odor persists strongly after shaking. Acidify a portion of the solution with $HC_2H_3O_2$ and add 1 or 2 drops $K_4Fe(CN)_6$ solution. The white precipitate is $Cd_2Fe(CN)_6$. To the remainder add dil. H_2SO_4 to acid reaction, then some iron filings and boil for a short time. Filter, acidify with dil. H_2SO_4, unless the solution is still acid, and pass H_2S into the liquid. The yellow precipitate is CdS.

The $Cu(OH)_2$ and $Cd(OH)_2$, though very slightly soluble in water, dissolves readily in ammonia, owing to the union of the Cu^{++} and Cd^{++} ions in the saturated solutions with NH_3 molecules to form the complex ions $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$. These complex cations have an extremely slight tendency to dissociation, and the simple ion concentration (Cu^{++} or Cd^{++}) in the solution is exceedingly low. Ammonium salts, however, owing to common ion effect, greatly reduce the OH^- ion concentration in the solution, and thus permit the Cu^{++} or Cd^{++} ion concentration, and therefore also the corresponding complex cation concentration, to attain a much higher value than in the saturated solutions of $Cu(OH)_2$ or $Cd(OH)_2$ in ammonia alone. In other words, the solubility of $Cu(OH)_2$ or $Cd(OH)_2$ in ammonia is greatly increased by the presence of ammonium salts. It should be noted that (in the case of cadmium, for example) the following distinct sets of equilibria are involved:

$$(1.)\ \underset{\text{(Solid)}}{Cd(OH)_2} \rightleftarrows \underset{\text{(Dissolved)}}{Cd(OH)_2} \rightleftarrows Cd^{++} + 2OH^-;$$

$$(2.)\ Cd^{++} + 4NH_3 \leftrightarrows Cd(NH_3)_4^{++};$$

$$(3.)\ NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-.$$

ANALYSIS.

II. Hydrogen Sulfide Group.

(5) General unknowns may contain considerable amounts of free acid, indicated by turning blue litmus paper a pink-red color. In all such cases, this excess of acid must be removed in order to completely precipitate the metallic ions of Group II. The presence of acetates may also interfere by causing the sulfides of Group III to precipitate along with Group II.

Removal of Excess Acid.—Add to the solution in a small Pyrex beaker 5 or 6 cc. conc. HNO_3 and evaporate nearly to dryness (that is, to a paste), taking care not to bake any of the residue. Excessive heating would cause As and Hg to be lost by volatilization, and Sn and perhaps some other metals might be rendered insoluble in HCl. Moisten the residue with 2 or 3 cc. conc. HCl and evaporate again almost to dryness. Add to the residue 4 cc. dil. HCl and a little water. Boil gently until solution is complete, dilute to 40 cc. and treat according to the paragraph below headed "Precipitation."

The proper acidity for the precipitation of Group II may also be obtained by adding water or dil. HCl, as the case may be, to the solution until a drop on a stirring rod gives a blue-green color when placed on a mark made by a "copying" pencil on glazed (not filter) paper. If the acid is too concentrated, the color will be yellow; if too dilute, blue. The "copying" pencils contain, as a pigment, methyl violet, which belongs to the group known as indicators.

Precipitation.—Heat the solution, which should contain 4 cc. dil. HCl, and which should have a volume of 40 cc., in a small conical flask nearly to boiling, add 1 cc. NH_4I solution,[1] and saturate hot with H_2S for not less than 5 minutes. *This is best accomplished by passing the H_2S delivery tube through a one-hole rubber stopper fitting the mouth of the flask. The gas is allowed to pass for a moment to expel the air in the flask and the stopper is then forced into place. The H_2S can now enter the flask only as it is used in the precipitation. The flask must not, of course, be heated while the stopper is in place. Precipitation is hastened by shaking the flask.* Cool, add without filtering 60 cc. cold water, completely saturate the mixture in the cold with H_2S, cork the flask, shake it, and allow to stand for a short time.

a. *No precipitate forms.*—Group II is absent. Treat the solution according to (**16.**).

b. *A fine white precipitate (sulfur) is formed.*—If the solution has changed in color from reddish-yellow to green, the presence of a chromate is indicated; if it has changed from purple to almost colorless the presence of a permanganate is indicated. Group II is absent. Filter and treat the filtrate according to (**16.**).

When oxidizing substances, like ferric salts, are present, H_2S is largely oxidized to sulfur and also to some extent to H_2SO_4. Barium, if present, is thereby precipitated as $BaSO_4$, and this may therefore also be contained in the precipitate. Hence, although barium does not belong to Group II, provision must be made for its detection here, since if present in small quantity all of it may have been removed from the solution at this point. The fine white precipitate is therefore filtered off and boiled (together with the filter) with strong Na_2CO_3 solution, which changes the $BaSO_4$ to $BaCO_3$. This is filtered off, washed, dissolved by pouring a little dil. HCl through the filter, the solution is heated to boiling, and and then 1 or 2 cc. dil. H_2SO_4 are added, and the mixture is allowed to stand. A white precipitate is $BaSO_4$.

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[1] The NH_4I hastens the precipitation by reducing the arsenic from As^{V} to As^{III}, which reacts much more rapidly with H_2S.

c. *A colored precipitate is formed.*—This may contain HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, SnS, SnS_2, and also it may contain sulfur and a very little $BaSO_4$. Filter, and wash the precipitate thoroughly with hot water, rejecting the washings. Treat the filtrate according to (**16.**). Treat the precipitate as described in (**6.**) unless it is known that the copper group alone is present, in which case treat the sulfides at once according to (**7.**).

(**6.**) **Separation of the Copper and Tin Groups.**—Transfer the precipitate (along with the filter paper, if necessary) to a small flask, add 5 to 10 cc. $(NH_4)_2S_x$, and warm very gently for ten minutes with frequent shaking (**do not boil**). Dilute with an equal volume of water, filter, and if there is a residue, wash it once with hot water. In order to ascertain whether the tin group has been completely removed, warm a small portion of the residue in a test-tube with 1 cc. water and 5 to 10 drops $(NH_4)_2S_x$ solution, dilute with 1 or 2 cc. water, filter, and make distinctly acid with dil. HCl. If the precipitate is finely divided and nearly white, the separation is known to be sufficiently complete; if, however, the precipitate is colored,[1] warm the main residue again with 5 to 10 cc. $(NH_4)_2S_x$, as above, and filter, but keep this filtrate separate from the first one.

a. *The colored precipitate dissolves completely in* $(NH_4)_2S_x$. The copper group is absent. Treat the solution according to (**12.**). If there should be left a very minute quantity of a very light colored residue, insoluble in $(NH_4)_2S_x$, it should be at once examined for barium according to (**5.**)b.

b. *A colored residue is left.* The copper group is present. Treat the residue according to (**7.**); treat the $(NH_4)_2S_x$ filtrate according to (**12.**).

(**7.**) **Mercuric Mercury.**—Wash the $(NH_4)_2S_x$ residue thoroughly with hot water, to which, if the solid tends to run through the filter, add 2 or 3 grams of solid NH_4NO_3. Transfer the residue, which may contain HgS, PbS, Bi_2S_3, CuS, CdS, ($BaSO_4$ and SnS), to a small beaker, add 10 to 20 cc. of a mixture of one volume HNO_3 (sp. gr. 1.20) and two volumes water, cover the beaker with a watch glass and boil gently for 2 or 3 minutes. Filter and wash. Treat the filtrate by (**8.**). Boiling HNO_3 of this concentration dissolves the sulfides of lead, bismuth, copper, and cadmium very quickly. Hardly any HgS is dissolved, unless the boiling is long continued, in which case the acid becomes more concentrated, black HgS is dissolved in part, and the remainder is converted into a heavy white compound, $Hg(NO_3)_2.2HgS$. Any SnS not extracted by the $(NH_4)_2S_x$ solution, is converted by the HNO_3 into metastannic acid, most of which remains undissolved (if much cadmium is present and tin is in the stannous state, as much as 15 mg. of the latter may be wholly left in the $(NH_4)_2S_x$ residue).[1]

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[1] A pronounced yellow color indicates arsenic or tin, and an orange-red color indicates antimony. Darker colored precipitates sometimes consist of mixtures of the sulfides of this subgroup, though their color may be due to traces of CuS (or of HgS), which are very slightly soluble in $(NH_4)_2S_x$, and which are reprecipitated, along with sulfur, upon acidifying the solution.

Transfer the HNO_3 residue, with the filter if necessary, to a test-tube, add 2 or 3 cc. conc. HCl and 4 or 5 drops conc. HNO_3, and boil, adding more HNO_3 if necessary. Dilute to 10 or 15 cc., filter, add to the filtrate *clear* $SnCl_2$ solution, at first drop by drop, and finally 2 or 3 cc. A white or gray precipitate shows the presence of mercury.

(**8.**) **Lead.**—To the filtrate containing Pb, Bi, Cu, Cd (and Ba) as nitrates, add 2 or 3 cc. conc. H_2SO_4, and evaporate in a Pyrex beaker until dense white fumes of H_2SO_4 just begin to come off. Cool and pour cautiously into a small beaker containing 15 cc. cold water, rinsing out the dish with the same solution. Shake, cool again, and allow to stand 4 or 5 minutes. Filter, wash the precipitate with dil. H_2SO_4 and then with a little water. Treat the filtrate by (**9.**). $PbSO_4$ is fairly soluble in dil. HNO_3[1] (or HCl) and therefore, to insure complete precipitation of lead, the HNO_3 must be entirely removed by evaporation. A finely divided, white precipitate indicates the presence of lead or of barium; but a coarsely crystalline precipitate may be due to bismuth—$(BiO)_2SO_4$. (If such a precipitate has separated with the $PbSO_4$, filter, treat the filtrate by (**9.**), and dissolve the precipitate by pouring repeatedly through the filter a 10 cc. portion of hot dil. HCl, receiving the filtrate in a small Pyrex beaker. Add 10 cc. dil. H_2SO_4, evaporate to H_2SO_4 fumes as before, cool and pour into 10 or 15 cc. of cold water. Add the filtrate to the solution reserved for (**9.**). The precipitate will now consist of $PbSO_4$ only.)

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[1] If it is necessary to recover any tin which may be present in the HNO_3 residue, transfer the latter to a poreclain dish, add 20 to 40 cc. saturated bromine water, cover the dish, and warm gently under a hood for 5 to 10 minutes, with frequent stirring. Boil to expel the bromine, filter, cool the solution, and add to it a few drops of dil. HCl. Test the solution for mercury with $SnCl_2$ solution as described above. Bromine water dissolves HgS, but leaves in the residue any metastannic acid. (If the residue is still dark colored, extract it with a fresh portion of bromine water to remove the rest of the HgS, filter, and reject the filtrate.) Warm the residue gently with 2 cc. $(NH_4)_2S_X$ solution, dilute with 2 cc. of water, filter, and add the solution to the main $(NH_4)_2S_X$ extract obtained in (**6.**).

Pour repeatedly over the $PbSO_4$ precipitate on the filter a hot 10 to 20 cc. portion of 10 per cent. $NH_4C_2H_3O_2$ solution. To the filtrate add a little $K_2Cr_2O_7$ solution and 3 or 4 cc. $HC_2H_3O_2$. A yellow precipitate is $PbCrO_4$. $(BiO)_2SO_4$ dissolves in $NH_4C_2H_3O_2$ solution and gives a yellow precipitate with $K_2Cr_2O_7$; but this precipitate, unlike $PbCrO_4$, is soluble in $HC_2H_3O_2$. If a white residue, insoluble in $NH_4C_2H_3O_2$, remains, it should be tested for barium according to (**5.**) b.

(9.) Bismuth.—To the solution, containing Bi, Cu and Cd as sulfates, add NH_4OH until its odor persists strongly after shaking. Shake to coagulate the precipitate $Bi(OH)_3$, filter, and wash. Treat the filtrate by (**10.**). Pour over the precipitate a little freshly prepared Na_2SnO_2 solution. A black residue is metallic bismuth. This test is extremely delicate: if the $Bi(OH)_3$ from just enough bismuth to produce a hardly visible turbidity is collected on a white filter and tested with Na_2SnO_2, the black color is very apparent.

(10.) Copper.—If the filtrate from (**9.**) is blue, copper is present. Acidify one-fourth of the solution with $HC_2H_3O_2$, add 2 or 3 drops $K_4Fe(CN)_6$ solution, and allow to stand five minutes. A red precipitate (or coloration) is $Cu_2Fe(CN)_6$. Treat the remainder of the solution by (**11.**). Cadmium is precipitated by $K_4Fe(CN)_6$ as white $Cd_2Fe(CN)_6$, but this does not hide the pink color of the $Cu_2Fe(CN)_6$, provided very little $K_4Fe(CN)_6$ is added; the copper salt is less soluble, and hence it precipitates first.

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[1] 10 grams of pure 11 per cent. HNO_3 dissolve 33 mg. PbSO.

(**11.**) **Cadmium.**—If copper is absent, add dil. H_2SO_4 just to acid reaction, and pass H_2S through the solution. A yellow precipitate is CdS. If copper is present, add dil. H_2SO_4 till the deep blue color disappears, then some iron filings, boil for a short time, filter from the iron filings, and, unless the solution is still acid, just acidify it with dilute H_2SO_4, and pass into it H_2S. A yellow precipitate is CdS.

If, owing to previous errors in the analysis, a black precipitate (containing HgS, CuS, FeS, etc.) is obtained at this point, filter it off, wash it, and boil it with a mixture of 3 cc. dil. H_2SO_4 and 10 cc. water; filter, dilute the filtrate, and test it with H_2S. The diluted H_2SO_4 is without action upon HgS or CuS, it changes PbS to insoluble $PbSO_4$, and it dissolves CdS (and FeS).

B. The Tin Group.

PRELIMINARY EXPERIMENTS.

Arsenic in Arsenious Compounds.—Use a solution of As_2O_3 in HCl. (Such a solution contains, besides arsenious acid, a small quantity of unhydrolyzed $AsCl_3$, which ionizes according to the equation $AsCl_3 \rightleftarrows As^{+++} + 3Cl^-$.) Precipitate with H_2S, warming the solution. Filter, put the precipitate into a test-tube by means of a spatula, add a little $(NH_4)_2S_x$ and warm gently. The As_2S_3 dissolves as ammonium thio-arsenate, $(NH_4)_3AsS_4$. (Compare with the formula of ammonium arsenate.) Add dil. HCl to acid reaction, filter, wash and heat the As_2S_5 obtained for several minutes in about 10 cc. of $(NH_4)_2CO_3$ solution just below the boiling point. (The equation for this reaction may be omitted.) To this ammoniacal solution add 3 or 4 cc. of H_2O_2 solution, and concentrate the mixture to about 5 cc. by boiling in a Pyrex beaker. Transfer to a test-tube, heat almost to boiling and, by means of a funnel and filter paper,[1] filter into the solution a few cc. of "magnesia mixture" (*i. e.*, $MgCl_2 + NH_4Cl$) and sufficient conc. NH_4OH (sideshelf) to make the mixture decidedly alkaline. Shake vigorously. If the precipitate does not appear immediately, allow the tube to stand an hour or more. The precipitate is $MgNH_4AsO_4$.

Arsenic in Arsenic Compounds.—Use a solution of potassium arsenate, K_3AsO_4. Pass H_2S into the cold solution, and note that no precipitate forms. Add 2 or 3 cc. of dilute HCl, warm and saturate again with H_2S. A precipitate forms, but very slowly. Now heat a fresh portion of the solution nearly to boiling, add 2 or 3 cc. of concentrated HCl and a few drops of NH_4I solution,[2] and pass H_2S into the hot solution. The arsenic is precipitated in this case mainly as $As_2S_3 + 2S$. From this point, the procedure would be the same as in the preceding paragraph.

Antimony.—Use a solution of $SbCl_3$. Warm, precipitate with H_2S, filter, and dissolve the Sb_2S_3 in $(NH_4)_2S_x$. The Sb is now in the form of ammonium thio-antimonate, $(NH_4)_3SbS_4$. Acidify the solution with dil. HCl. Orange Sb_2S_5 is precipitated. Filter and warm the Sb_2S_5 with 10 cc. of $(NH_4)_2CO_3$ solution. (Only traces of Sb_2S_5 are dissolved.) Filter, boil the precipitate with 10 cc. of conc. HCl, dilute to about 25 cc. and filter out any insoluble residue (sulfur). Transfer the filtrate to a small beaker and add about .05 gram of metallic aluminium. Allow to stand until all of the Al is dissolved. Filter out the black deposit of metallic Sb, transfer it to a beaker and dissolve in 4 or 5 cc. of conc. HCl to which a few drops of conc. HNO_3 have been added. Boil to decompose excess HNO_3, filter if necessary, dilute to about 100 cc., and pass H_2S. The orange precipitate is Sb_2S_3.

Tin in Stannous Compounds.—Use a solution of $SnCl_2$. Warm precipitate with H_2S, filter, wash, dissolve in $(NH_4)_2S_x$ and add dil. HCl to the solution. The precipitate is now SnS_2. Filter, and heat the precipitate almost to boiling with about 10 cc. $(NH_4)_2CO_3$ solution. (Compare effect with As and Sb.) Filter, boil the precipitate with 10 cc. of conc. HCl, filter out any insoluble residue (sulfur), and add 0.3 to 0.5 gram of metallic zinc. Allow to stand until all of the zinc is dissolved and any gray tin which may have separated out redissolves. Filter, if necessary, dilute the solution with one-half its volume of water, and pour it at once into 5 cc. of $HgCl_2$ solution. The white precipitate is Hg_2Cl_2; this, of course, shows the presence of Sn.

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[1] The magnesia mixture reagent tends to develop a precipitate upon standing, and should always be filtered before using.

[2] See footnote, p. 24.

Tin in Stannic Compounds.—If $SnCl_4$ solution is used instead of $SnCl_2$ in the above experiments, the results are the same, except that the first precipitate in this case is SnS_2; SnS and SnS_2 both dissolve in $(NH_4)_2S_x$ to form $(NH_4)_2SnS_3$.[1]

ANALYSIS.

(12.) Dilute in a small flask the first portion of the $(NH_4)_2S_x$ solution with 20 cc. of water, add to it dil. HCl until it reacts acid after shaking, and warm it slightly for five minutes with shaking to coagulate the precipitate.

a. *A finely divided* (not flocculent) *white or pale yellow precipitate is obtained.* The tin group is probably absent. Ammonium polysulfide gives a precipitate of finely divided sulfur upon the addition of HCl, according to the equation: $(NH_4)_2S_x + 2HCl \rightarrow 2NH_4Cl + H_2S + (x - 1)S$.

b. *A flocculent yellow or orange precipitate is obtained.* The tin group is present. (Treat the second portion of the $(NH_4)_2S_x$ solution in the same way, and unite the precipitate, if the sulfides of the tin group are present in it, with the first one.) Filter, and wash the precipitate, using suction; and finally suck it as dry as possible.[2] Reject the filtrate; treat the precipitate by **(13.)**.

c. *A buff-colored, brown, or dark gray precipitate is obtained.* A buff color indicates the presence of copper, a dark gray indicates that of mercury, both of whose sulfides are slightly soluble in $(NH_4)_2S_x$. The tin group may or may not be present.

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[1] SnS is insoluble in ammonium monosulfide, $(NH_4)_2S$; by ammonium polysulfide it is converted into SnS_2, which then reacts with the excess of the reagent to form $(NH_4)_2SnS_3$.

[2] In case a suction pump is not at hand, the precipitate may be freed from excess of moisture by pressing the filter containing it between several thicknesses of clean filter paper.

(13.) Arsenic.—Introduce the precipitate, which may contain As_2S_5, Sb_2S_5, SnS_2, S and sometimes small amounts of HgS and CuS (along with the filter paper, if necessary) into a small beaker, add 10 or 15 cc. of $(NH_4)_2CO_3$ solution, along with an equal volume of water, and heat to a temperature just below the boiling point for several minutes, stirring frequently. Filter, reserving the residue for (**14.**). Acidify the filtrate in a small beaker with dil. HCl. The precipitate is As_2S_5. If the amount of this precipitate is large, the $(NH_4)_2CO_3$ extraction should be repeated upon the residue above, and the second As_2S_5 precipitate (if any) added to the first. Wash, dissolve the precipitate in a few cc. NH_4OH and add to the solution 4 or 5 cc. of H_2O_2 solution, which converts the dissolved As_2S_5 to $(NH_4)_3AsO_4$. The solution is then evaporated to a volume of 5 cc. or less in a Pyrex beaker and transferred to a test tube. By means of a funnel and filter paper, filter into this solution conc. NH_4OH (sideshelf) until the solution is distinctly alkaline, and then, using the same paper, a few drops of "magnesia mixture." Shake vigorously. If no precipitate forms, rub the walls of the test-tube with the end of a stirring rod. Do not decide that the test is negative until the tube has stood an hour or more. Reserve this solution for the second paragraph of (**14.**). The presence of As in the $MgNH_4AsO_4$ precipitate may be confirmed by dissolving it, after filtering, by pouring a little dil. HCl through the filter, heating the filtrate nearly to boiling, adding a few drops of NH_4I, and passing H_2S for at least five minutes into the hot solution. A white precipitate turning yellow shows the presence of As.

(14.) Antimony.—Wash the residue from (**13.**), and add 10 cc. of hot conc. HCl. Filter out any residue of As_2S_5 and S, receiving the filtrate in a small beaker. Dilute to about 25 cc. and add about 0.5 gram of metallic aluminium. When the Al is completely dissolved, warm and filter, reserving the filtrate for (**15**). Dissolve the black residue in 4 or 5 cc. of conc. HCl to which a few drops of conc. HNO_3 have been added. Dilute to a convenient volume, filter if necessary, pass H_2S, warm and shake, so as to coagulate the precipitate. A distinctly orange precipitate indicates Sb. A milky-to-yellow color may be caused by sulfur or the incomplete removal of the As.

If the above test for Sb is negative, the filtrate from the $MgNH_4AsO_4$ precipitate (**13.**) should be tested for Sb by acidifying with dil. HCl and passing H_2S. Small amounts of Sb that might otherwise be overlooked may be detected in this way.

(**15.**) **Tin.**—Dilute the filtrate from (**14.**) to 8 or 10 cc. and pour it at once into a test-tube containing 5 cc. $HgCl_2$ solution. A white precipitate of Hg_2Cl_2 shows the presence of Sn.

GROUP III.

AMMONIUM SULFIDE GROUP.

This group contains the metals whose sulfides, though soluble in dilute acids, are insoluble in water in the presence (or absence) of ammonium salts. These metals are all precipitated from neutral solution by $(NH_4)_2S$; zinc, manganese, iron, cobalt, and nickel are precipitated as sulfides, while chromium and aluminium, owing to hydrolysis, are precipitated as hydroxides by $(NH_4)_2S$. Fe^{+++}, Al^{+++}, and Cr^{+++} are precipitated as hydroxides upon the addition of NH_4OH, even in the presence of ammonium salts; Fe^{++}, Co^{++}, Ni^{++}, Mn^{++}, and Zn^{++}, in the presence of ammonium salts, are not precipitated by NH_4OH (but in the presence of air, iron and manganese, owing to oxidation, are slowly precipitated), unless phosphates, etc., are present.

In the presence of phosphates, borates, oxalates, fluorides, etc., calcium, strontium, barium, and magnesium may also be precipitated with this group upon the addition of NH_4OH.

This group is divided into two subgroups:

A. The Aluminium Group.—To this belong **aluminium, chromium,** and **zinc,** whose hydroxides are readily soluble in a mixture of NaOH and Na_2O_2 (or H_2O_2).

B. The Iron Group.—To this belong **manganese, iron, cobalt,** and **nickel,** whose hydroxides are insoluble in a mixture of NaOH and Na_2O_2 (or H_2O_2).

PRELIMINARY EXPERIMENTS.

Aluminium.—To an aluminium salt solution add NH_4Cl, boil and add NH_4OH. Filter, wash, and dissolve the precipitate in a little dil. HCl. Dilute the solution to 10 or 15 cc., make it alkaline with NaOH solution, cool, and add 1 or 2 grams solid Na_2O_2, with stirring (the $Al(OH)_3$ will dissolve just as well in an excess of NaOH, without the addition of Na_2O_2). Boil, acidify the solution containing $NaAlO_2$ with dil. HNO_3, and add gradually to the hot solution NH_4OH until the solution is strongly alkaline towards litmus paper. In order to distinguish $Al(OH)_3$ from silicic acid, H_2SiO_3, which is frequently present in small amounts as an impurity in alkaline reagents, dissolve the $Al(OH)_3$ in dil. HCl and carefully evaporate to dryness in a Pyrex beaker. Moisten the residue with a few drops of conc. HCl, dilute, filter and add NH_4OH. The $Al(OH)_3$ is reprecipitated. This treatment converts the silicic acid into SiO_2, which does not dissolve again in HCl, and consequently gives no reaction with NH_4OH.

Chromium.—To a chromium salt solution add NH_4Cl, boil, and add NH_4OH until the liquid smells of it after shaking. Filter, wash, dissolve the precipitate in a little dil. HNO_3. Dilute the solution to 10 or 15 cc., make it alkaline with NaOH solution, cool, and add 1 or 2 grams solid Na_2O_2, in small portions, with stirring. Note change in color. Boil to decompose the excess of Na_2O_2, acidify the solution containing Na_2CrO_4 with dil. HNO_3, and add to the hot solution an excess of NH_4OH. Acidify the resulting solution with $HC_2H_3O_2$, and add $BaCl_2$. The yellow precipitate is $BaCrO_4$. Dissolve it, after filtering, in a very little dil. HNO_3, add 9 or 10 volumes of water, and to a portion of the cold solution in a test-tube add about 2 cc. ether and 1 cc. H_2O_2 and shake. The blue compound is a perchromic acid, probably H_3CrO_7. It is very unstable; by its decomposition oxygen is evolved and the chromium is reduced to a chromic salt. Its decomposition is greatly accelerated by an excess of H_2O_2, by the presence of much acid, and by raising the temperature.

Acidify a solution of $K_2Cr_2O_7$ with HCl, and saturate it with H_2S. Boil, filter, add NH_4Cl and NH_4OH. What is the precipitate? Account for the change in the color of the solution.

Zinc.—To a zinc salt solution add NH_4Cl, and NH_4OH in excess; then add H_2S. Warm, filter, dissolve the precipitate of ZnS in dil. HCl, boil to expel the H_2S (why expel it?), dilute to 10 or 15 cc., and add NaOH in excess. Acidify the solution containing Na_2ZnO_2 with dil. HNO_3, and add NH_4OH in excess.

Acidify the solution containing $[Zn(NH_3)_4](NO_3)_2$ with $HC_2H_3O_2$, and pass into it H_2S. The precipitate is ZnS. The presence of Na_2O_2 or other strong oxidizing agent may cause the separation of a white precipitate of sulfur at this point, which might be mistaken for ZnS. Remove the S by adding dil. HCl to acid reaction, and boiling to coagulate the undissolved S. Filter, add to the filtrate NH_4OH in excess. and pass H_2S. The second precipitate will be pure ZnS.

Manganese.—Dilute a little manganese salt solution with water, boil to expel the dissolved air, and divide into two portions. To the first, add NH_4OH. What is the precipitate? To the second, add several cc. of NH_4Cl solution, boil again, and then add NH_4OH. Explain the difference. Now cool both tubes and shake for some time so as to saturate the solutions with air. The brown precipitate is $MnO(OH)_2$.

To a fresh portion of the same solution add an equal volume of NH_4Cl solution, boil, add NH_4OH, then saturate with H_2S, warm, and filter. Dissolve the precipitate in a little dil. HCl, boil to expel H_2S, dilute the solution to 10 or 15 cc., make it alkaline with NaOH solution, cool, and add 1 or 2 grams solid Na_2O_2, in small portions, with stirring. Filter off and wash the precipitate of $MnO(OH)_2$, transfer it to a Pyrex beaker, add 10 or 15 cc. conc. HNO_3, heat to boiling, add not more than 0.5 gram of solid $KClO_3$ and boil gently for 2 or 3 minutes. ($MnO(OH)_2$ is not soluble in HNO_3, particularly in the presence of $KClO_3$, which is added to oxidize any of the lower oxides of nitrogen back to HNO_3.) Filter off the precipitate with an asbestos filter, made by pouring a suspension of washed asbestos over a compact plug of glass wool in a glass funnel. Transfer the precipitate to a porcelain dish, add 1 or 2 grams PbO_2, and about 10 cc. dil. HNO_3; boil for a short time, pour the mixture into a test-tube, and allow the excess of PbO_2 to settle. The solution is violet red in color, owing to the presence of $HMnO_4$.

$MnO(OH)_2$ (*e. g.*, stains on glass vessels) is easily soluble in dil. HNO_3 to which 1 or 2 cc. of H_2O_2 solution have been added.

Iron.—Saturate an acid solution containing a ferric salt with H_2S, boil to expel H_2S, filter, and add to the filtrate containing Fe^{++} ions NH_4OH to alkaline reaction, and then a little $(NH_4)_2S$. Filter off and wash the precipitate, dissolve it in a little dil. HCl, dilute to 10 or 15 cc., and make the solution alkaline with NaOH; then add about 1 gram solid Na_2O_2. The $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$ by the Na_2O_2. Dissolve the precipitate, after filtering, in dil. HCl, and divide the solution into three portions. To one add NH_4OH; to another add $K_4Fe(CN)_6$ solution; and to the third add NH_4SCN solution. The two precipitates are $Fe(OH)_3$ and $Fe_4[Fe(CN)_6]_3$, respectively, and the third portion of the solution is colored red, owing to the formation of un-ionized $Fe(SCN)_3$. This test may be made in the presence of much HCl, for HSCN is also a highly ionized acid, which is therefore not displaced from its salt. Much HNO_3 must not, however, be present: for, by its action on NH_4SCN, NO_2, which also gives a deep red color with NH_4SCN, may be formed. The test is extremely delicate, and if only a faint red color is obtained, the acids used must be tested for iron.

Cobalt.—To a cobalt salt solution add NH_4Cl and NH_4OH, then saturate with H_2S. Filter, wash, add to the precipitate 5 cc. dil. HCl and stir. Then add about 1 cc. dil. HNO_3 and warm. Make the resulting solution alkaline with NaOH, and then add about 1 gram solid Na_2O_2. The precipitate is $Co(OH)_3$; dissolve it in conc. HNO_3, to which 2 or 3 drops of NH_4NO_3[1] solution have been added, dilute and to the $Co(NO_3)_2$ solution add NH_4OH in excess. Acidify with $HC_2H_3O_2$ and divide into two portions.

Evaporate the first portion in a small beaker to a volume of 2 or 3 cc., transfer to a test-tube, add 1 or 2 cc. of NH_4SCN solution, and 1 or 2 cc. of amyl alcohol-ether mixture. Shake well. The blue-green color is due to $(NH_4)_2Co(SCN)_4$, which is easily soluble in amyl alcohol-ether mixture. The color does not appear with dilute solutions of cobalt salts.

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[1] The presence of ammonium salts in some way catalyzes the action of HNO_3 on $Co(OH)_3$.

To the second portion add a few drops of dimethylglyoxime solution. The brown color shows the presence of cobalt salts. (No equation need be written.)

Nickel.—With a nickel salt solution, perform the same experiments as given above under cobalt. The following important differences should be noted: Green $Ni(OH)_2$ is not oxidized to black $Ni(OH)_3$ by Na_2O_2; nickel salts give no reaction with NH_4SCN; with dimethylglyoxime, they give a bright red precipitate, easily soluble in strong acids.

The Effect of the Presence of Phosphates, Borates, Oxalates, etc., upon the Precipitation of Group III.—Dissolve a little solid $Ca_3(PO_4)_2$ in a few cc. dil. HCl, and add to the solution NH_4Cl, NH_4OH to alkaline reaction, and pass H_2S. The precipitate is $Ca_3(PO_4)_2$. Try the same experiment with a solution of $CaCl_2$ or $Ca(NO_3)_2$. Explain the formation of the $Ca_3(PO_4)_2$ precipitate.

ANALYSIS.

III. Ammonium Sulfide Group.

(16.) Precipitation.—Boil the filtrate from Group II (**5.**) until the H_2S is expelled. If phosphates, oxalates, borates and fluorides [1] are known to be absent, proceed directly to the fourth paragraph of this section. If they may be present, test small portions of the original solution for these anions. (See Anion Analysis.) Of these, phosphates and oxalates are the more common. The tests for these two anions are:

Test for Phosphate.—To a small portion of the solution add about 5 cc. of $(NH_4)_2MoO_4$ solution and 2 or 3 cc. conc. HNO_3 and warm. A yellow precipitate indicates the presence of phosphate (or arsenate).

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[1] When phosphate, fluoride, borate, or oxalate is present, magnesium, calcium, strontium, barium and managanese salts containing these anions mav be precipitated by NH_4OH. Fluoride will ordinarily have been removed, however, in the evaporation with acids in the preparation of the solution. (See Part II, page 96.) The borates of the alkaline earth elements are not sufficiently insoluble, particularly in the presence of ammonium salts, to be precipitated, unless they are present in large quantity.

Test for Oxalate.—Place a little MnO_2 in a test-tube fitted with a thistle tube and a delivery tube, and through the thistle tube introduce a small portion of the solution, which has been previously acidified with about 5 cc. of dilute H_2SO_4 and boiled to expel CO_2. Warm and pass any gas evolved through $Ca(OH)_2$. A milky white precipitate indicates the presence of oxalate.

Transfer the solution (see first paragraph, this section) to a flask, add NH_4OH until the solution is alkaline to litmus paper, and then 3 or 4 cc. more. Note the appearance of any precipitate that may be formed. Then saturate with H_2S. Shake the mixture and heat it nearly to boiling (to coagulate the precipitate). Filter off the precipitate and wash it with warm water. Test the filtrate with a little $NH_4OH + H_2S$ to insure complete precipitation of Group III. If there is a precipitate, unite it with the preceding one. Treat the precipitate by (**17.**) and the filtrate by (**24.**).

The H_2S is boiled out, and the effect produced by NH_4OH alone is noted, because it often gives a useful indication as to what elements are present. Instead of adding $(NH_4)_2S$ to the alkaline solution, H_2S is passed into it because in this way the solution of any NiS is entirely prevented. (If, however, it is preferred to use $(NH_4)_2S$, and the filtrate is brown or nearly black, the NiS may be precipitated from it by boiling the solution for a few minutes. It should then be united with the main precipitate.)

(17.) Separation of The Aluminium and Iron Groups.—Transfer the $(NH_4)_2S$ precipitate (with the filter if necessary) to a Pyrex beaker; add 5 to 20 cc. dil. HCl, according to the size of the precipitate, stir for a minute in the cold and then boil the mixture; if a black residue remains, add to the mixture a few drops conc. HNO_3 and boil again. Add a little water, filter from any sulfur, and evaporate the filtrate to 1 or 2 cc. to remove most of the acid. Dilute the solution to 15 to 20 cc.; make it alkaline with NaOH solution (avoiding a large excess), and if the precipitate is very large add 10 to 20 cc. more water. Cool the mixture, and add to it 1 or 2 grams solid Na_2O_2, in small portions with constant stirring. Then add 5 cc. 10 per cent. Na_2CO_3 solution, unless the alkali earth metals are known to be absent. *Boil to decompose the excess of* Na_2O_2, cool, and dilute with an equal volume of water.

a. *No precipitate is obtained.* The iron group is absent. Treat the solution by (**18.**).

b. *A precipitate is obtained.* Filter it off (with suction, if possible), and wash it with hot water. Treat the filtrate by (**18.**); the precipitate by (**21.**).

All the hydroxides and all the sulfides of the group, except CoS and NiS, usually dissolve readily in cold, dil. HCl. The fact that these two sulfides dissolve so much less readily in dilute acids than the others seems to be due to an unusually slow rate of solution, and not to a lesser solubility in water. By NaOH, Fe, Mn, Co and Ni are completely precipitated and do not dissolve in excess, while the hydroxides of Al, Cr, and Zn, being amphoteric substances, are soluble in a sufficient excess, forming with the NaOH aluminate ($NaAlO_2$), chromite ($NaCrO_2$), and zincate (Na_2ZnO_2). Upon the addition of Na_2O_2, $Fe(OH)_2$ is changed to $Fe(OH)_3$, $Mn(OH)_2$ to hydrated MnO_2, $Co(OH)_2$ to $Co(OH)_3$, and $Ni(OH)_2$ remains unchanged, all of which are insoluble in excess of NaOH. The $NaCrO_2$ in the solution is changed by Na_2O_2 into Na_2CrO_4, which remains in solution. The Na_2CO_3 is added in order to completely precipitate any alkali earth metals which may be present; it also decomposes the chromates of these metals, *and if it is not added, chromium may remain in the precipitate and escape detection.*

THE ALUMINIUM GROUP.

ANALYSIS.

(**18.**) **Aluminium.**—Acidify the alkaline filtrate from (**17.**) with HNO_3, avoiding a large excess; add NH_4OH till the solution is distinctly alkaline to litmus paper, and then add 2 or 3 cc. more to keep the zinc in solution. Heat to boiling, filter if there is a precipitate, and wash it thoroughly with hot water. Treat the filtrate by (**19.**). Dissolve the precipitate in 5 cc. dil. HCl, and evaporate just to dryness in a Pyrex beaker. Moisten the residue with a few drops of conc. HCl, dilute, filter, add excess of clear NH_4OH and heat to boiling. A precipitate is $Al(OH)_3$.

(**19.**) **Chromium.**—Acidify the filtrate from (**18.**) with $HC_2H_3O_2$, avoiding a large excess. The presence of 1 mg. chromium as chromate in 100 cc. of solution makes the solution distinctly yellow; therefore, if the solution is colorless, chromium is absent.[1] In that case, proceed at once to (**20.**). If, however, the solution is at all yellow, add about 10 cc. 10 per cent. $BaCl_2$ solution, allow the mixture to stand for 5 minutes, filter, and treat the filtrate by (20). A yellow precipitate is $BaCrO_4$; unless the precipitate is distinctly yellow, the following confirmatory test must be tried. Pour repeatedly through the filter containing the precipitate a cold mixture of 1 cc. dil. HNO_3 and 9 cc. water; to the cold solution in a test-tube add about 2 cc. ether and 1 cc. 3 per cent. H_2O_2 solution, and shake. Chromium is present if the ether layer is colored blue.

(**20.**) **Zinc.**—Warm the acetic acid solution from (**19.**) to about 50°, saturate it in a small flask with H_2S, cork the flask and allow it to stand for 10 minutes if no precipitate separates at once. Sometimes a precipitate of sulfur, more or less discolored by traces of metallic sulfides, appears at this point, due to incomplete separation of Na_2O_2, chromates, etc. Confirm Zn by adding dil. HCl to the mixture, boiling for a short time, and filtering. Now add NH_4OH to the filtrate and pass H_2S. A white precipitate is ZnS.

THE IRON GROUP.

ANALYSIS.

(**21.**) **Manganese.**—Transfer the precipitate from (**17.**)—which may contain $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, and possibly Ba, Sr, Ca and Mg in the form of carbonates, phosphates, etc.—to a Pyrex beaker, add 10 to 20 cc. conc. HNO_3 and a few drops of NH_4NO_3 solution, heat to boiling and add about 0.5 gram of solid $KClO_3$ and boil gently. A dark brown or black residue shows the presence of manganese. Filter it off through an asbestos filter, prepared by placing a small plug of glass wool in a funnel and pouring over it a little asbestos suspended in water. Wash thoroughly with hot water, combine the first washings with the main filtrate, and reserve for (**23.**). Transfer the residue (or a small part of it, if it is large) to a Pyrex beaker, add 1 or 2 grams of PbO_2 and about 10 cc. dil. HNO_3; boil for 1 or 2 minutes, and then pour the mixture into a test-tube and allow the PbO_2 to settle. A violet-red color indicates the presence of manganese.

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[1] In artificial light, a yellow solution may appear colorless.

(**22.**) **Iron.**—The procedure to be followed depends upon whether complicating anions, like phosphate, oxalate, etc., are present or not.

a. *Phosphate, oxalate, borate and fluoride are absent.*—Make the HNO_3 solution from (**21.**) strongly alkaline with NH_4OH, using an excess of 4 or 5 cc. A dark red precipitate is $Fe(OH)_3$. Filter and treat the filtrate by (**23.**). Wash the precipitate, dissolve it in dil. HCl and to one-half of the solution add $K_4Fe(CN)_6$ solution. A blue precipitate is caused by Fe^{+++}. To the other half add NH_4SCN, which will give a deep red color if iron is present.

b. *Phosphate, oxalate, etc., are present.*—Test one-tenth of the HNO_3 solution from (**21.**) for iron by evaporating it just to dryness, adding 1 or 2 cc. HCl, and evaporating again to decompose the HNO_3. (HNO_3 gives a red color with NH_4SCN that might be mistaken for a test for Fe^{+++}.) Dilute the solution to 10 cc. and add a few cc. of NH_4SCN solution. A permanent red color indicates the presence of iron. To the remainder of the solution from (**21.**) slowly add NH_4OH until the precipitate just fails to redissolve on shaking. (If, owing to the addition of too much NH_4OH a large precipitate separates or the solution becomes alkaline, make it distinctly acid with $HC_2H_3O_2$.) Add 5 cc. 50% $NH_4C_2H_3O_2$ solution and, unless the mixture is already brownish-red, add $FeCl_3$[1] drop by drop, with stirring, until such a color is produced. Dilute the mixture to about 100 cc., boil for 5 minutes in a 250 cc. flask, adding more water if a very large precipitate is formed, and allow the mixture to stand for a short time. Filter while still hot, rejecting the precipitate. Add 4 or 5 cc. more $NH_4C_2H_3O_2$ solution to the filtrate, boil, and if a precipitate forms, filter it off on a fresh filter and reject it. Make the filtrate alkaline with NH_4OH, adding an excess of 2 or 3 cc.; filter off and reject any precipitate. Saturate the filtrate with H_2S, warm and filter, reserving the filtrate for (**23a.**). Wash the precipitate, dissolve it a few cc. dil. HCl, to which have been added a few drops of conc. HNO_3, and filter out any sulfur residue. Add excess NH_4OH, and proceed to (**23.**).

(**23**) **Nickel and Cobalt.**—Divide the filtrate from (**22.**) into two parts. To the first add dimethylglyoxime solution. The red precipitate shows the presence of nickel, and a brown solution or filtrate shows cobalt.

Acidify the second portion with $HC_2H_3O_2$, and evaporate to 1 or 2 cc. in a small beaker. Transfer to a test-tube, add an equal volume of NH_4SCN solution, and 1 or 2 cc. of amyl alcohol-ether mixture. Shake vigorously. The blue-green layer indicates cobalt.

(**23a.**) Add to the solution from (**22b.**) dil. HCl just to acid reaction, and evaporate the mixture to a volume of 25 or 30 cc.; filter from any sulfur. To the filtrate add NH_4OH drop by drop until its odor persists after shaking; heat to boiling; add $(NH_4)_2CO_3$ solution as long as a precipitate continues to form, and then allow the mixture to stand for 10 minutes.

a. *No precipitate forms.* Add to the clear solution a few drops each of $(NH_4)_2SO_4$, and $(NH_4)_2C_2O_4$ solution, and warm. Filter from any precipitate, and test *the whole filtrate* for magnesium by (**26.**). Since this solution is known to contain potassium (See (**21**)), it should then be rejected.

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[1] The purpose of the excess of Fe^{+++} is to preferentially combine with the PO_4^{---} ion, leaving the alkaline earth ions in solution. For example: $Ca_3(PO_4)_2 + 2\,FeCl_3 \rightarrow 3\,CaCl_2 + 2\,FePO_4$. The completeness of this reaction is due to the high insolubility of $FePO_4$.

b. *A precipitate may contain* $BaCO_3$, $SrCO_3$ and $CaCO_3$. Filter, and wash the precipitate with hot water. Test the filtrate for magnesium according to the preceding paragraph; to the precipitate on the filter add any precipitate which may be obtained in (**24.**) (by filtering it off through the same filter), and analyze the mixture by (**25.**).

GROUP IV.

AMMONIUM CARBONATE GROUP.

To this group belong **barium, strontium,** and **calcium,** whose hydroxides and sulfides are not precipitated in the presence of ammonium salts, but whose carbonates are precipitated in the presence of ammonium salts. The hydroxides of these metals are soluble with difficulty in water, but are quite readily soluble in the presence of ammonium salts. (The hydroxide and carbonate of magnesium are practically insoluble in water, but they dissolve readily if ammonium salts are present.)

PRELIMINARY EXPERIMENTS.

Barium.—To about 5 cc. of a boiling barium salt solution add $(NH_4)_2CO_3$ solution, allow the mixture to settle, filter, and dissolve the precipitate by repeatedly pouring a hot 5 cc. portion of 30 per cent. $HC_2H_3O_2$ solution through the filter. To one-third of the solution add an equal volume of a clear saturated solution of $CaSO_4$; notice whether $BaSO_4$ is formed immediately or not. To the remainder of the solution, diluted to 75 or 100 cc., add $K_2Cr_2O_7$, and filter (the filtrate should be yellow in color). The precipitate is $BaCrO_4$. Filter, and test the filtrate for barium with NH_4OH and $(NH_4)_2CO_3$. Dissolve the $BaCrO_4$ in dil. HCl, add 0.5 cc. alcohol, and boil until the solution has become light green in color; neutralize the boiling solution with NH_4OH, and filter off from the $Cr(OH)_3$. Evaporate the filtrate nearly to dryness, and introduce a little of it, on a clean platinum wire, into the colorless flame of a Bunsen burner. The green color is due to the barium.

Strontium.—To about 5 cc. of a boiling solution containing strontium add $(NH_4)_2CO_3$ solution, allow the mixture to settle, filter, and dissolve the precipitate in $HC_2H_3O_2$ as described under

Barium. To one-third of the solution add an equal volume of saturated $CaSO_4$ solution, warm, if necessary, and notice the difference between the behavior of barium and strontium. Dilute the remainder of the solution to about 100 cc., add $K_2Cr_2O_7$, then NH_4OH and $(NH_4)_2CO_3$; filter, and wash the precipitate of $SrCO_3$. Dissolve the $SrCO_3$ in $HC_2H_3O_2$, and test one-third of the solution with $CaSO_4$ solution. To the remainder add $(NH_4)_2SO_4$ in slight excess, boil, filter, and add to the filtrate NH_4OH to alkaline reaction, and then a little $(NH_4)_2C_2O_4$. Introduce a little of a concentrated solution of $SrCl_2$, on a clean platinum wire, into the flame of a Bunsen burner, and note the effect.

Calcium.—Use a solution of $CaCl_2$. Try the same experiments as with strontium. The last precipitate is calcium oxalate, CaC_2O_4.

If a spectroscope is available, study carefully the spectrum of each metal of the group, using saturated solutions of the chlorides,

ANALYSIS.

IV. Ammonium Carbonate Group.

(24.) Precipitation.—Add to the solution from **(16.)** or to the filtrate from **(22b.)** dil. HCl just to acid reaction, and evaporate the mixture to a volume of 25 or 30 cc.; filter off any sulfur. To the filtrate add NH_4OH drop by drop until its odor persists after shaking; heat to boiling; add $(NH_4)_2CO_3$ solution as long as a precipitate continues to form, and then allow the mixture to stand for 10 minutes.

a. *No precipitate forms.* Absence of more than traces of barium, strontium, or calcium. Divide in two portions. To one add a few drops $(NH_4)_2SO_4$ solution and warm. A precipitate is $BaSO_4$. To the other add a very little $(NH_4)_2C_2O_4$ solution and warm. A precipitate is CaC_2O_4. Reunite the two portions, filter off from any precipitate, and treat the filtrate by **(26.)**.

b. *A precipitate may contain* $BaCO_3$, $SrCO_3$, and $CaCO_3$. Filter,[1] and wash the precipitate. To the filtrate add a few drops each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ solutions, noting if either gives a precipitate; heat to boiling; filter, rejecting any precipitate; and treat the filtrate by (**26.**). Dissolve the $(NH_4)_2CO_3$ precipitate by repeatedly pouring a hot, 5 to 10 cc. portion of 30 per cent. $HC_2H_3O_2$ solution through the filter, and test the solution as follows:

---

[1] See **(23a.)**.

(**25.**) Add to a small portion of the solution in acetic acid an equal volume of saturated $CaSO_4$ solution.

a. *No precipitate forms even after some time and warming.* Ba and Sr are absent. Confirm the presence of Ca by adding to the remainder of the solution a little $(NH_4)_2C_2O_4$ solution. A white pulverulent precipitate is CaC_2O_4.

b. *A precipitate forms slowly or after warming.* Ba is absent. Sr is present. Dilute the remainder of the solution to 20 or 25 cc., heat to boiling, add $(NH_4)_2SO_4$ solution as long as a precipitate continues to form, boil for 2 or 3 minutes, and filter off the $SrSO_4$ (and $CaSO_4$). To the filtrate, which may contain $CaSO_4$, add NH_4OH to alkaline reaction, and then a little $(NH_4)_2C_2O_4$ solution. A white precipitate, forming immediately and in appreciable amount, is CaC_2O_4.[1] Filter it off, ignite a little of it on a *clean* platinum wire, barely moisten the residue on the wire with HCl, and test it in the flame.

c. A *precipitate forms immediately.* Ba is present. Dilute the remainder of the solution to about 100 cc., add 5 cc. saturated $NaC_2H_3O_2$ solution, heat to boiling, and add gradually $K_2Cr_2O_7$ solution until it is present in slight excess. Boil, and filter while boiling hot (the filtrate should be yellow in color). The precipitate is $BaCrO_4$. Apply to it the confirmatory flame test described under barium in the preliminary experiments. To the filtrate add NH_4OH to alkaline reaction, heat to boiling, and add $(NH_4)_2CO_3$ solution in excess. A precipitate may contain $SrCO_3$ and $CaCO_3$.

---

[1] In the absence of calcium and in the presence of strontium, a very slight precipitate of SrC_2O_4 forms, especially upon standing. This may be distinguished from the real calcium test by a "control" experiment: that is, by adding $(NH_4)_2C_2O_4$ to a little $CaSO_4$ solution and comparing with the test obtained upon the unknown.

Filter it off (rejecting the filtrate), wash it, and dissolve it on the filter in a little hot $HC_2H_3O_2$. To a small portion of the solution add $CaSO_4$ solution, and boil. If a precipitate of $SrSO_4$ forms, treat the remainder of the solution as in b. If strontium is absent, test the remainder of the solution for calcium with NH_4OH and $(NH_4)_2C_2O_4$ solution.

The analysis of this group by the method here given does not permit an estimate to be formed as to the relative quantities in which the members of the group are present.[1] The method is based entirely upon the relative solubilities of the sulphates, chromates, and oxalates of the metals. In the following table are given, *in milligrams*, the amounts of the salts that are held in solution at 18° by 1 liter of pure water. The solubility is of course less in the presence of an excess of a common-ion. The arrows emphasize the order of increasing solubility.

	CO_3	CrO_4	SO_4	C_2O_4	$(OH)_2$
Ba	23	3.8	2.3	86. ↑	37000 ↑
Sr	11	1200	110	46.	7700
Ca	13	4000 ↓	2000 ↓	5.6	1700

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[1] If it is desired to form such an estimate, dissolve the precipitate of $SrCO_3$ and $CaCO_3$ (obtained with $(NH_4)CO_3$ after the removal of the Ba) in a few cc. dil. HNO_3, evaporate the solution to dryness in a small porcelain dish, and heat strongly on an iron plate until no odor of HNO_3 can be detected After cooling, at once rub the contents of the dish to a powder with the blunt end of a glass rod, add 5 cc. absolute alcohol and 5 cc. absolute ether, and triturate with the rod for 2 or 3 minutes. Filter and wash the residue on the filter with small portions of the alcohol-ether mixture until the last washings show no turbidity with a drop of dil. H_2SO_4. The residue is $Sr(NO_3)_2$; dissolve it in water and add $(NH_4)_2CO_3$ solution. Evaporate the ether-alcohol filtrate and washings to dryness on a steam bath. The residue is $Ca(NO_3)_2$; dissolve it in water and add $(NH_4)_2CO_3$ solution.

GROUP V.

SOLUBLE GROUP.

To this group belong **magnesium, sodium, potassium,** and **ammonium.** There is no common precipitant for the group and very few insoluble salts of the last three metals are known.

PRELIMINARY EXPERIMENTS.

Magnesium.—To one portion of a magnesium salt solution add an equal volume of NH_4Cl, and then add NH_4OH. To another portion add NH_4OH directly; then add NH_4Cl and shake. Explain the results according to the ionic theory. Perform the same experiment, using $(NH_4)_2CO_3$ solution in the place of NH_4OH.

To a solution containing Mg^{++} ions add NH_4OH to alkaline reaction, NH_4Cl solution until the precipitate of $Mg(OH)_2$ is dissolved, and then a little Na_2HPO_4 solution, and shake. The precipitate is $MgNH_4PO_4$.

Sodium.—Use a solution of NaCl. Test in the flame with a clean platinum wire. Add 1 drop of NaCl solution to 10 drops of KCl solution and make the flame test. The flame test for sodium is so sensitive that only when the yellow color is intense and persistent is sodium likely to be present in appreciable quantity. See if the color is visible through a cobalt glass.

Dilute 3 cc. of NaCl solution with an equal volume of water, and add a few drops of $HClO_4$ solution. Does a precipitate form? Now add a volume of alcohol equal to that of the dilute solution, and then add a few drops of fluosilicic acid, H_2SiF_6. The gelatinous precipitate is Na_2SiF_6, insoluble in 50% alcohol.

To a small amount of KCl solution add the alcohol and the H_2SiF_6 solution as in the preceding paragraph. What is the precipitate in this case? Can the test for sodium be used without previously removing the potassium?

Potassium.—Use a solution of KCl. Clean a platinum wire by dipping it in conc. HCl solution in a test-tube, and heating in the Bunsen flame until the color produced is only momentary. Now dip in the KCl solution and make the flame test. See if any color is visible through a cobalt glass.

To a small amount of KCl solution in a test-tube add several drops of $HClO_4$ solution. The precipitate is $KClO_4$, insoluble in cold, but fairly soluble in hot water.[1]

Ammonium.—Use a solution of NH_4Cl. Test in the flame, using a platinum wire.

Now warm a small quantity of NH_4Cl solution in a small beaker with some NaOH solution, covering the beaker with a watch glass to the lower side of which a piece of red litmus paper is stuck by means of a few drops of water. Also note the odor evolved.

Dilute a little NH_4Cl solution with an equal volume of water, as in the case of sodium, and add a few drops of $HClO_4$ solution. No precipitate forms, since NH_4ClO_4 is soluble in water. Now add alcohol and H_2SiF_6 solution. If no precipitate forms, add a little NH_4OH solution and warm, if necessary. The precipitate seems to be $(NH_4)_2SiF_6$, which is only fairly soluble in 50% alcohol. The presence of NH_4 salts sometimes interferes with the H_2SiF_6 test for sodium, apparently in this way.

To some NH_4Cl solution in a Pyrex beaker add 1 or 2 cc. conc. HNO_3, evaporate to dryness and ignite strongly. If any residue remains, cool, moisten with conc. HNO_3, and repeat the evaporation and heating. Write equations for the reactions involved.

ANALYSIS.

V. SOLUBLE GROUP.

(26.) Magnesium.—Evaporate the solution from **(24.)** which may contain the members of this group, in a Pyrex beaker until ammonium salts begin to crystallize out. Acidify the liquid with HCl, filter, and add to about one-fourth of the filtrate in a test-tube a third its volume of NH_4OH and 1 or 2 cc. Na_2HPO_4 solution. Shake vigorously for 2 or 3 minutes, and if no precipitate appears, rub the sides of the tube with a glass rod (see the remarks in (**13.**) in regard to the precipitation of arsenic as $MgNH_4AsO_4$). A white *crystalline* precipitate is $MgNH_4PO_4$; if flocculent, the precipitate may be $AlPO_4$, which may be present here (owing to the solubility of $Al(OH)_3$ in NH_4OH) if too large a quantity of NH_4OH was used in the precipitation of Group III.

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[1] Concerning the delicacy of this test, the addition of one-fourth its volume of $HClO_4$ (sp. gr. 1.12) to a portion of 0.1 normal KCl produces a distinct precipitate of $KClO_4$; if to 10 cc. of 0.25 normal KCl solution 0.5 cc. $HClO_4$ is added, a good test is obtained. The addition of 0.05 cc. $HClO_4$ to a 10 cc. portion of normal KCl solution gives an instantaneous precipitate.

(**27.**) To the remainder of the solution from (**26.**) add 2 or 3 cc. conc. HNO_3 and evaporate to dryness in a small Pyrex beaker. Cool the beaker, moisten the residue with a few drops of conc. HNO_3, evaporate again and then heat strongly to expel ammonium salts. Allow the beaker to cool and dissolve the residue in 3 to 5 cc. hot water. Filter, if necessary, through a small filter paper. Try the flame test, both without and with the cobalt glass. A persistent yellow color indicates sodium, while a purplish color (seen through the cobalt glass) indicates potassium.

(a) **Potassium.**—Cool the solution thoroughly and add $HClO_4$ solution in slight excess. A white crystalline precipitate of $KClO_4$ indicates potassium. Filter on a small paper and wash with 1 or 2 cc. of cold water, adding the washings to the main filtrate. Test for the completeness of the precipitation by adding a drop or two more of the $HClO_4$ solution.

(b) **Sodium.**—To the filtrate from (a) above add an equal volume of alcohol and then a few drops of H_2SiF_6. A white gelatinous precipitate, Na_2SiF_6, indicates sodium.

(**28.**) **Ammonium.**—Test a portion of the *original substance* for ammonium salts by mixing it in a small beaker with an excess of NaOH solution. Cover the beaker with a watch glass, on the under side of which is placed a piece of moist red litmus paper, and warm gently. If the litmus turns blue, ammonium salts are present. In that case, the odor of NH_3 will generally be perceptible. Care must be taken that the litmus paper does not absorb any of the alkaline NaOH solution, and for that reason the mixture should be only gently heated; *do not boil it.*

OUTLINES OF CATION ANALYSIS.

The following tables give the analytical procedures for the cations in outline form. They are valuable in study (particularly, in review) by showing the fundamental steps in skeleton form, stripped of most of the details. The student is warned, however, that they are not sufficient for a laboratory guide in an actual analysis. In such work, the foregoing detailed procedures must be followed:

TABLE I. SEPARATION OF GROUPS.

Dilute the unknown solution to 40 cc. and add 4 cc. dil. HCl. Filter and wash the precipitate.

<table>
<tr><td rowspan="4">Precipitate:
Group I
(as chlorides).
See Table II.</td><td colspan="4">Filtrate—Saturate with H_2S. Filter, wash precipitate.</td></tr>
<tr><td rowspan="3">Precipitate:
Group II
(as sulfides).
See Table III.</td><td colspan="3">Filtrate—Add NH_4OH+H_2S. Filter, wash precipitate.</td></tr>
<tr><td rowspan="2">Precipitate:
Group III
(as sulfides and hydroxides).
See Table VI.</td><td colspan="2">Filtrate—Add $(NH_4)_2CO_3$. Filter, wash precipitate.</td></tr>
<tr><td>Precipitate:
Group IV
(as carbonates).
See Table X.</td><td>Filtrate:
Group V.
See Table XI.</td></tr>
</table>

TABLE II. ANALYSIS OF GROUP I.

Solution: Neutral or slightly acid solution, containing Group I and subsequent groups. Add 4 cc. dil. HCl. Filter, wash with cold water.

<table>
<tr><td colspan="3">Precipitate: $PbCl_2$, $AgCl$, Hg_2Cl_2. Wash with hot water.</td><td rowspan="3"><i>Filtrate:</i>
Groups
II,
III,
IV,
V.

See
Table III.</td></tr>
<tr><td rowspan="2">Solution: $PbCl_2$.

Add $K_2Cr_2O_7$.
Add. H_2SO_4
Precipitate:
[illegible] & white
Yellow $PbCrO_4$.</td><td colspan="2">Residue: $AgCl$, Hg_2Cl_2. Extract with NH_4OH.</td></tr>
<tr><td>Filtrate: $Ag(NH_3)_2Cl$.
Add HNO_3.

Precipitate:

White $AgCl$.</td><td>Residue:
add aqua regia
& the dilute
Black
$HgNH_2Cl + Hg$.
[illegible]
for a [illegible]</td></tr>
</table>

TABLE III. PRECIPITATION OF GROUP II AND SEPARATION OF COPPER AND TIN SUB-GROUPS.

Solution: Filtrate from Group I (or unknown in Group II), containing 4 cc. of dil. HCl in a volume of 40 cc. Heat, add 1 cc. NH_4I, pass H_2S, dilute, pass H_2S, filter, wash. with hot

<table>
<tr><td colspan="3">Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, Sb_2S_3, SnS, SnS_2. Wash, digest in warm $(NH_4)_2S_x$.</td><td rowspan="3">Filtrate:

Groups
III,
IV,
V.

See
Table VI.</td></tr>
<tr><td rowspan="2">Residue: HgS, PbS, Bi_2S_3, CuS, CdS.

See Table IV.</td><td colspan="2">Filtrate: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$. Acidify with dil. HCl. Filter.</td></tr>
<tr><td>Precipitate:

As_2S_5, Sb_2S_5, SnS_2, S.
See Table V.</td><td>Filtrate:

NH_4Cl.
Reject.</td></tr>
</table>

TABLE IV. ANALYSIS OF THE COPPER SUB-GROUP.

2) Residue from the $(NH_4)_2S_x$ extraction: *HgS*, *PbS*, *Bi_2S_3*, *CuS*, *CdS*. Boil with dil. HNO_3 (dil. HNO_3 + 2 volumes of water). Filter, wash.

<table>
<tr>
<td rowspan="6">Residue:
HgS,
S.
Dissolve in aqua regia, boil out excess acid and filter out any S.
½ Dilute, add $SnCl_2$.
Gray Prec.:
$Hg_2Cl_2 - Hg$.
½ Add copper + polish
KI [illegible]</td>
<td colspan="4">Filtrate: Pb, Bi, Cu and Cd as nitrates. Add H_2SO_4, evapo- 4) rate to H_2SO_4 fumes. Dilute, filter.</td>
</tr>
<tr>
<td rowspan="5">Prec.:
$PbSO_4$.
Dissolve in NH_4Ac.
Add $K_2Cr_2O_7$, HAc.
Prec.:
Yellow *$PbCrO_4$*.</td>
<td colspan="3">Filtrate: Bi, Cu, Cd as sulfates. Add NH_4OH, (5) filter.</td>
</tr>
<tr>
<td rowspan="4">Prec.:
$Bi(OH)_3$
Add Na_2SnO_2.
Residue:
Black *Bi*.</td>
<td colspan="2">(6)
Filtrate: $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$ as sulfates. If blue, proceed to (A). If indecisive, divide. Acidify smaller portion with HAc, add $K_4Fe(CN)_6$. Precipitate (or rose color): $Cu_2Fe(CN)_6$. If Cu is found, treat remaining solution by (A); if Cu is absent, proceed directly to (B).</td>
</tr>
<tr>
<td colspan="2">(A) Add H_2SO_4, Fe filings, boil, and filter.</td>
</tr>
<tr>
<td>Prec.:
Cu – Fe.
Reject.</td>
<td>Filtrate: $CdSO_4$, $FeSO_4$.
Treat by (B).</td>
</tr>
<tr>
<td colspan="2">7) (B) Acidify with H_2SO_4, pass H_2S. Precipitate: Yellow *CdS*.</td>
</tr>
</table>

TABLE V. ANALYSIS OF THE TIN SUB-GROUP.

Precipitate: As_2S_5, Sb_2S_5, SnS_2, S. Wash with warm water as long as the wash water is darkened by $PbAc_2$. Add $(NH_4)_2CO_3$, warm, filter. Repeat the extraction with $(NH_4)_2CO_3$, and combine filtrates.

<table>
<tr><td colspan="2" rowspan="2">Filtrate: As_2S_5 (+ trace of Sb_2S_5) dissolved in $(NH_4)_2CO_3$.
Acidify with dil. HCl, filter, wash.
Precipitate: As_2S_5 (+ Sb_2S_5).
Dissolve in NH_4OH, add H_2O_2, concentrate, filter into magnesia mixture, allow to stand.</td><td colspan="3">Residue: Sb_2S_5, SnS_2, S (+ As_2S_5). Wash. Add 10 cc. hot conc. HCl. Dilute, filter, wash.</td></tr>
<tr><td colspan="2">Filtrate: $SbCl_3$, $SnCl_4$. Dilute, add Al. Filter, wash.</td><td rowspan="2">Residue:
As_2S_5, S.
Reject.</td></tr>
<tr><td>Precipitate:
White $MgNH_4AsO_4$.</td><td>Solution:
$(NH_4)_3SbO_4$.
Add HCl, boil, pass H_2S.
Precipitate:
Orange Sb_2S_3.</td><td>Residue: Sb.
Dissolve in aqua regia, boil, dilute, pass H_2S.
Orange Sb_2S_{3-5}.</td><td>Filtrate: $SnCl_2$ (+ $AlCl_3$). Pour into $HgCl_2$.
Precipitate:
White Hg_2Cl_2.</td></tr>
</table>

TABLE VI. PRECIPITATION OF GROUP III AND SEPARATION OF ALUMINIUM AND IRON SUB-GROUPS.

Solution: Filtrate from Group II or unknown solution in Group III. If filtrate from Group II, boil to expel H_2S; if not, add 5 cc. NH_4Cl and omit the boiling. Unless phosphates and oxalates are known to be absent, take two small samples and test for these anions, reserving main part of the solution for the subsequent procedures.

To 1st portion add 2 or 3 cc. conc. HNO_3 and 5 cc. $(NH_4)_2MoO_4$. Warm.	Place a little MnO_2 in a test-tube generator (see Anion Analysis) and introduce through the thistle tube 2nd portion and 5 cc. dil. H_2SO_4. Warm and pass gas evolved through $Ca(OH)_2$.
Yellow precipitate indicates phosphate.	Milky white precipitate indicates oxalate.

To the main portion of the solution add NH_4OH. Precipitate: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_{2-3}$; also Ba, Sr, Ca and Mg as oxalates and phosphates if these anions are present. Solution: $MnCl_2$, and Zn, Co and Ni as NH_3-complexes. Without filtering, saturate with H_2S. Filter, wash.

<table>
<tr>
<td colspan="2">Precipitate: $Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, CoS, NiS; also Ba, Sr, Ca and Mg as oxalates and phosphates. Add HCl and boil. Dissolve any black residue (due to CoS, NiS) by adding dil. HNO_3 to the HCl mixture and boiling. Filter out any S. Add NaOH, Na_2O_2 and Na_2CO_3 (if alkaline earths are present). Boil, dilute, filter, wash.</td>
<td rowspan="2">Filtrate:
Groups IV, V.
See Table X.</td>
</tr>
<tr>
<td>Filtrate:
$NaAlO_2$,
Na_2CrO_4,
Na_2ZnO_2.
See Table VII.</td>
<td>Residue: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, also Ba, Sr, Ca and Mg as oxalates and phosphates.
See Tables VIII, IX.</td>
</tr>
</table>

TABLE VII. ANALYSIS OF ALUMINIUM SUB-GROUP.

Solution: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2. Add HNO_3, NH_4OH, heat to boiling. Filter.

<table>
<tr>
<td rowspan="2">Precipitate: $Al(OH)_3$; H_2SiO_3 as impurity.

Filter, wash, dissolve in dil. HCl, evaporate. Add conc. HCl, warm, dilute, filter. Add NH_4OH.

Precipitate:

White, gelatinous $Al(OH)_3$.</td>
<td colspan="2">Filtrate: Na_2CrO_4 (yellow), $Zn(NH_3)_4(OH)_2$. Add HAc. Solution: $Na_2Cr_2O_7$ (orange), $ZnAc_2$. Add $BaCl_2$. Filter.</td>
</tr>
<tr>
<td>Precipitate:

Yellow $BaCrO_4$.

If color is not distinct, dissolve in dil. HNO_3, add ether and H_2O_2.

Blue layer indicates Cr.</td>
<td>Filtrate: $ZnAc_2$. Warm, saturate with H_2S.

Precipitate:

White $ZnS + S$ (?).

Add dil. HCl, evaporate, add water, filter. Add NH_4OH, H_2S.

Precipitate: White ZnS.</td>
</tr>
</table>

TABLE VIII. ANALYSIS OF IRON SUB-GROUP (IN THE ABSENCE OF PHOSPHATES, OXALATES, ETC.).

Residue: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$. Add conc. HNO_3, NH_4NO_3, heat to boiling, add $KClO_3$, boil gently. Filter on asbestos. Wash.

<table>
<tr>
<td rowspan="3">Residue:
Black $MnO(OH)_2$

Add PbO_2, dil. HNO_3, boil.

Solution:

Purple $HMnO_4$.</td>
<td colspan="3">Filtrate: Fe, Co, Ni as nitrates. Dilute, add NH_4OH. Filter, wash.</td>
</tr>
<tr>
<td rowspan="2">Precipitate:

$Fe(OH)_3$.

Dissolve in dil. HCl, add NH_4SCN.

Solution:

Red $Fe(SCN)_3$.</td>
<td colspan="2">Filtrate: Co and Ni as NH_3 complexes. Divide into two portions.</td>
</tr>
<tr>
<td>To 1st portion add dimethylglyoxime.

Red precipitate: *Ni-dimethylglyoxime.*

Brown filtrate or solution indicates Co.</td>
<td>Acidify 2nd portion with HAc. Evaporate. Add NH_4SCN, amyl alcohol-ether mixture. Shake vigorously. Blue-green layer incates Co.</td>
</tr>
</table>

TABLE IX. ANALYSIS OF THE IRON SUB-GROUP (IN THE PRESENCE OF PHOSPHATES AND OXALATES.

Residue: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$; Ca, Sr, Ba, Mg as oxalates, phosphates and carbonates. Add conc. HNO_3, heat to boiling, add $KClO_3$, boil gently. Filter on asbestos. Wash.

<table>
<tr>
<td rowspan="4">Residue:
$MnO(OH)_2$.
Add PbO_2, dil. HNO_3, boil.
Solution:
Purple $HMnO_4$.</td>
<td colspan="4">Filtrate: Fe, Co, Ni, Ba, Sr, Ca, Mg (as nitrates) and $H_2C_2O_4$ and H_3PO_4. Evaporate one-tenth, add water, and test for Fe^{+++} with NH_4SCN. To remainder add $FeCl_3$ (unless considerable Fe is present), NH_4OH, HAc, NH_4Ac; dilute and boil. Add NH_4OH. Filter, wash.</td>
</tr>
<tr>
<td rowspan="3">Precipitate:
$FePO_4$, $Fe(OH)_2Ac$.
Discard.</td>
<td colspan="3">Filtrate: Co, Ni, Ba, Sr, Ca, Mg, NH_4 salts. Add H_2S.</td>
</tr>
<tr>
<td colspan="2">Precipitate: CoS, NiS.
Dissolve in dil. aqua regia. Filter out S, evaporate. Dilute, add NH_4OH, divide into two parts.</td>
<td rowspan="2">Filtrate:
Ba, Sr, Ca, Mg as acetates.
See Tables X, XI.</td>
</tr>
<tr>
<td>To 1st portion add dimethylglyoxime.
Red precipitate: *Ni-dimethylglyoxime.*
Brown filtrate or solution indicates Co.</td>
<td>Acidify 2nd portion with HAc. Evaporate.
Add NH_4SCN, amyl alcohol-ether mixture. Shake vigorously.
Blue-green layer indicates Co.</td>
</tr>
</table>

Table X. Analysis of Group IV.

Solution containing Ba, Sr, Ca and possibly members of Group V. If filtrate from Group III, add HCl, evaporate to 25 cc.; if Group IV only, add 5 cc. NH_4Cl. Add NH_4OH, heat to boiling, add $(NH_4)_2CO_3$. Filter, wash.

<table>
<tr><td colspan="3">Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$. Dissolve in HAc. To a small sample of the solution add $K_2Cr_2O_7$. Yellow precipitate, $BaCrO_4$, indicates Ba. If Ba is present, proceed to (A). If Ba is absent, treat rest of solution by (B).</td><td rowspan="4">Filtrate:
Traces of Ba, Sr, Ca; Group V.
Add $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$, filter.
Filtrate:
Group V.
See Table X.</td></tr>
<tr><td colspan="3">(A) To the whole solution add $K_2Cr_2O_7$. Filter, wash.</td></tr>
<tr><td rowspan="2">Precipitate:
Yellow $BaCrO_4$.
Dissolve in HCl, evaporate to dryness, moisten with HCl.
Green flame indicates Ba.</td><td colspan="2">Filtrate: Sr and Ca acetates or chromates. Add $(NH_4)_2CO_3$. Filter, wash.</td></tr>
<tr><td>Filtrate:
K_2CrO_4.
Reject.</td><td>Precipitate: $SrCO_3$, $CaCO_3$.
Dissolve in HAc, and proceed to (B).</td></tr>
<tr><td colspan="4">(B) Solution: Sr and Ca as acetates. To a small sample of the solution add $CaSO_4$. Slight precipitate, $SrSO_4$, slowly forming, indicates Sr. If Sr is present, proceed to (C); if Sr is absent, proceed to (D).</td></tr>
<tr><td colspan="4">(C) Heat the remaining solution, add $(NH_4)_2SO_4$, filter.</td></tr>
<tr><td rowspan="2">Precipitate:
$SrSO_4$, $CaSO_4$.
Reject.</td><td colspan="3">Filtrate: Ca as sulfate. Proceed to (D).</td></tr>
<tr><td colspan="3">(D) To the solution add $(NH_4)_2C_2O_4$. White precipitate, forming immediately, insoluble in HAc: CaC_2O_4.</td></tr>
</table>

TABLE XI. ANALYSIS OF GROUP V.

Solution containing Mg, K, Na, NH_4 salts. If the solution is filtrate from Group IV, add $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$ to remove traces of Ba, Sr and Ca. Filter out any precipitate. Evaporate almost to crystallization. Filter. Acidify with dil. HNO_3. Divide as required below.

To ¼ of the solution add NH_4OH. If a precipitate forms, carefully redissolve in NH_4Cl. Filter the mixture, if not perfectly clear. Heat, add Na_2HPO_4. Shake vigorously. Precipitate: White $MgNH_4PO_4$.

To a larger portion of the solution add conc. HNO_3, evaporate to dryness in a Pyrex beaker. Cool, moisten with conc. HNO_3, ignite gently. Dissolve in water. Filter if necessary.

Solution: K and Na as nitrates. Try flame test. Violet, K; yellow, Na. Cool solution thoroughly, add $HClO_4$. Filter, wash.

Precipitate: White $KClO_4$. Flame test: Violet.	Filtrate: Na as nitrate. Add equal volume of alcohol, and a few drops of H_2SiF_6. White gelatinous precipitate: Na_2SiF_6.

Transfer the remainder of the solution (or a portion of the original unknown if NH_4 compounds have been introduced as reagents) to a small beaker, add NaOH and warm. NH_3 fumes, turning red litmus paper blue, indicate the presence of NH_4^+.

B. DETECTION OF THE NON-METALLIC IONS.

In most cases the non-metallic elements do not exist in solution in the form of simple anions containing only an atom of the single element (the most important ones which do occur in this manner are chlorine, bromine, iodine, and sulfur); they combine mostly with other elements to form compound anions such as CO_3^{--}, NO_3^{-}, PO_4^{---}, etc. It is therefore usual in the detection of the non-metals to first convert the elements into acids (unless they are already present in the form of simple or compound ions); these furnish anions which contain the elements in question, and which can be readily recognized by means of their characteristic reactions.

In the analysis of an unknown substance, the number of anions to be tested for is generally restricted by the solubility of the substance taken in connection with the metals already found in it. A substance soluble in water and containing a certain cation cannot contain any anion known to form an insoluble salt with that cation; for example, a soluble substance giving a neutral (or slightly acid) solution which contains Zn^{++} and Ba^{++} ions need not be tested for any of the following anions; $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, S^{--}, SO_3^{--}, CO_3^{--}, $C_2O_4^{--}$, $C_4H_4O_6^{--}$, PO_4^{---}, AsO_3^{---}, AsO_4^{---}, CrO_4^{--}, $S_2O_3^{--}$, SO_4^{--}, F_2^{--}, SiO_3^{--}, SiO_4^{----}, etc.[1] However, if a substance is insoluble, certain acid radicals forming soluble salts with the metals present may nevertheless be present; for such salts may be held back by certain insoluble substances (*e. g.*, $Ba(NO_3)_2$ by $BaSO_4$). Moreover, many basic salts are insoluble, although readily soluble when normal (*e. g.*, $Pb(OH)NO_3$). In order to determine what acid radicals are excluded by the solubility of the substance, the solubility of the various salts of the metals present must be considered. The table of solubilities on the back cover-sheet will be of assistance in this connection.

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[1] Exceptions to this principle appear in cases where substances or complexes of low ionization are formed; for example, the following sets of mixtures, all of which are soluble in water: $PbSO_4$ and excess $NH_4C_2H_3O_2$, AgCl and $Na_2S_2O_3$, HgI_2 and excess KI; $MgCO_3$ and NH_4Cl, etc.

GROUPS OF THE ANIONS.

The detection of the anions, unlike that of the cations, does not, in general, require their separation from one another. They are, nevertheless, divided into groups according to their behavior toward a few general reagents, which serve simply to show the presence or the absence of members of a whole group of anions, and not to separate one group from another. If a group is found to be absent, it is of course unnecessary to test for any anion in that group. But if a certain group is found to be present, every anion in that group which may be present (see p. 63) must be tested for.

The ordinary grouping of the anions depends on the solubility of their barium and silver salts in neutral and acid solutions. It is given in slightly modified form below.

Group I.—Anions whose silver salts are insoluble in water or dilute nitric acid; but whose barium salts are soluble in water. *Hydrochloric, hydrobromic, hydriodic, hydrocyanic, thiocyanic, hydroferrocyanic, hydroferricyanic* and *hydrosulfuric* (H_2S) *acids.*

Group II.—Anions whose silver salts are soluble in dilute nitric acid, but difficultly soluble in water; and whose barium salts are soluble in water. *Nitrous and acetic acids.*

Group III.—Anions whose silver and barium salts are insoluble in water, but soluble in dilute nitric acid.

a. Anions whose silver salts are colorless (white). *Sulfurous, carbonic, oxalic, boric, and tartaric acids.*

b. Anions whose silver salts are colored. *Phosphoric, arsenic, arsenious, thiosulfuric,*[1] *and chromic acids.*

Group IV.—Anions whose silver and barium salts are soluble in water. *Nitric, chloric, permanganic, acetic and nitrous acids.* $AgC_2H_3O_2$ and $AgNO_2$ are difficultly soluble (cf. Group II).

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[1] Thiosulfates give with silver nitrate a white precipitate of $Ag_2S_2O_3$, which soon decomposes, the color changing very rapidly, through yellow to black, Ag_2S being formed. (Certain other thiosulfates of heavy metals decompose in the same way.)

Group V.—Anions whose silver salts are soluble in water, but whose barium salts are insoluble in water or in dilute acids. *Sulfuric, and hydrofluoric acids.* BaF_2 is difficultly soluble in dil. HNO_3.

Group VI.—Anions of non-volatile acids, giving soluble alkali salts, which on evaporation and digestion with HCl give insoluble residues. *The silicic acids.*

Group VII—Anions of organic acids which carbonize on heating. *Tartaric acid, citric acid, acetic acid, malic acid, succinic acid, benzoic acid, salicylic acid, lactic acid, propionic acid, butyric acid, and hundreds of others.*

DETERMINATION OF GROUPS.

The reagents used in determining the anion groups that may be present in a solution of an unknown are $AgNO_3$ and $Ba(NO_3)_2$. These reagents are applied, separately, to small portions of the unknown solution; if precipitates form, their solubility in dilute HNO_3 is also tried.

The general relationship is shown in the following table:

Determination of Anion Groups

<table>
<tr><td colspan="4">Precipitated by $AgNO_3$</td><td colspan="2">Not precipitated by $AgNO_3$.</td><td rowspan="3"></td></tr>
<tr><td>$AgNO_3$ precipitate insoluble in dil. HNO_3.</td><td colspan="3">$AgNO_3$ precipitate soluble in dil. HNO_3.</td><td colspan="2"></td></tr>
<tr><td colspan="2">Not precipitated by $Ba(NO_3)_2$.</td><td colspan="2">$Ba(NO_3)_2$ gives a precipitate which is soluble in HNO_3.</td><td>Not precipitated by $Ba(NO_3)_2$.</td><td>$Ba(NO_3)_2$ gives a precipitate which is insoluble or nearly so in dil. HNO_3.</td></tr>
<tr><td>Group I.</td><td>Group II.</td><td colspan="2">Group III.</td><td>Group IV.</td><td>Group V.</td><td>Group VI.
See Part II.</td></tr>
<tr><td></td><td></td><td>*a.*
Ag salts, White</td><td>*b.*
Ag precipitate, colored:</td><td></td><td></td><td></td></tr>
<tr><td>Cl^-
Br^-
I^-
CN^-
CNS^-
$Fe(CN)_6^{==}$
$Fe(CN)_6^{\equiv}$
$S^=$</td><td>$C_2H_3O_2^-$
NO_2^-</td><td>$SO_3^=$
$CO_3^=$
$C_2O_4^=$
$BO_3^{\equiv}$
$C_4H_4O_6^=$</td><td>$PO_4^{\equiv}$
$S_2O_3^=$
$AsO_3^{\equiv}$
$AsO_4^{\equiv}$
$CrO_4^=$</td><td>NO_3^-
ClO_3^-
MnO_4^-
(NO_2^-)
$(C_2H_3O_2^-)$</td><td>$SO_4^=$
$Fe_3^=$</td><td>Silicic acids.</td></tr>
</table>

The following points should be carefully observed:

(a) The presence of the cations of the metallic groups I, II, III and IV do not interfere with the test for Anion Groups I, II and V; the cations of these metallic groups, however, must be removed before testing for the presence of Anion Group III. This follows from the fact that the anions of Group III form precipitates in neutral solution, in almost every case, with all the cations except Na^+, K^+, NH_4^+ and H^+, and consequently precipitation would occur upon making the solution neutral, thereby masking the effect of the $AgNO_3$ and $Ba(NO_3)_2$ reagents. It should be understood, on the other hand, that the presence of these "heavy" metals does not necessarily interfere with testing for the *individual members* of this group.

(b) These reagents give no indication of the presence or absence of Group IV. Consequently these anions—NO_3^- and $C_2H_3O_2^-$ in particular—must be tested for in all solutions.

(c) The $Ba(NO_3)_2$ reagent, especially if it is in concentrated form, may give a precipitate of $Ba(NO_3)_2$ with high concentrations of nitrates, causing the student to infer the presence of Groups III or V. The solubility of such a precipitate in water should always be tried.

(d) Certain anions, whose acids are either very volatile or else unstable, are not to be looked for in acid solution. They are CN^-, S^{--}, NO_2^-, CO_3^{--}, $S_2O_3^{--}$.

(5) The color of the precipitate obtained with $AgNO_3$ is a very significant indication of the presence of certain anions. The colors are as follows: $AgCl$, $AgCN$, $Ag_4Fe(CN)_6$, Ag_2SO_3, Ag_2CO_3, $Ag_2C_2O_4$, Ag_3BO_3, $Ag_2C_4H_4O_6$ are white; $AgBr$ cream-colored; AgI yellow; $Ag_3Fe(CN)_6$ orange; Ag_2S black; Ag_3PO_4 yellow; Ag_3AsO_3 yellow; Ag_3AsO_4 reddish-brown; Ag_2CrO_4 dark red. $Ag_2S_2O_3$ is really white, but speedily undergoes hydrolysis, giving black Ag_2S. (For fuller details, see table, "Reactions of the Acid Ions," pp. 88–93.)

PRELIMINARY EXPERIMENTS.

Reactions with Concentrated H_2SO_4.—Many anions give more or less characteristic reactions upon the addition of concentrated H_2SO_4 to the dry (or better, moist) substance.

Chlorides.—Place a little solid NaCl in a test-tube, moisten with a drop of water, and add about 1 cc. of concentrated H_2SO_4. Test the gas evolved by a drop of $AgNO_3$ solution on a piece of glass tubing. Note the appearance of the precipitate.

Bromides.—Moisten a little KBr in a test-tube as above, and add concentrated H_2SO_4. What is the primary reaction in this case? Explain the formation of the brown fumes.

Iodides.—Add concentrated H_2SO_4 to a moistened crystal of KI. Write equations showing the formation of I_2, SO_2, S and H_2S from HI and H_2SO_4.

Cyanides.—When H_2SO_4 is added to a soluble cyanide (*e. g.*, KCN), HCN is evolved, recognized by its odor. (*Caution!* This gas is extremely poisonous. The student should not try this experiment, except under the direct supervision of an instructor.)

Thiocyanates.—To a little solid NH_4SCN (or KSCN) add a few drops of concentrated H_2SO_4. A gas containing $HCHO_2$ (formic acid), CO_2, COS and SO_2, is evolved, and a precipitate of S separates. (No equation to be written.)

Sulfides.—Add a little H_2SO_4 to a crystal (or a little saturated solution) of Na_2S. Explain the formation of SO_2 in this reaction.

Acetates.—Add a little concentrated H_2SO_4 to some solid $NaC_2H_3O_2$ in a test-tube. Note the odor.

Nitrites.—Add concentrated H_2SO_4 to a little solid KNO_2. Compare the amount of brown fumes evolved by adding the acid to an approximately equal amount of KNO_3.

Sulfites.—Add concentrated H_2SO_4 to a little moistened Na_2SO_3. Carefully smell the gas.

Thiosulfates.—Add a little concentrated H_2SO_4 to some moistened $Na_2S_2O_3$. Note the odor of the gas evolved, and the separation of the S precipitate.

Carbonates.—To a little Na_2CO_3 add concentrated H_2SO_4. What is the gas evolved?

Oxalates.—Add concentrated H_2SO_4 to about 1 gram of $Na_2C_2O_4$ and warm gently. Set fire to the gas, and note the color of the flame. Repeat the experiment, only using dilute instead of concentrated H_2SO_4. Is there any action in this case?

Tartrates.—Moisten a small amount of $Na_2C_4H_4O_6$ with water, and add concentrated H_2SO_4. The blackening is due to the separation of C (carbonization). The gas evolved contains SO_2, formed by the reduction of some of the acid. (No equations to be written.)

Chlorates.—Place a crystal (or a very small amount of the powder) of $KClO_3$ in a test-tube, and by means of a pipette add a drop or two of concentrated H_2SO_4. A greenish gas, ClO_2, is evolved and colors the H_2SO_4 intensely yellow. (*Care!* Large amounts of $KClO_3$ might cause a serious explosion.) Balance the equation: $KClO_3 + H_2SO_4 \rightarrow KHSO_4 + KClO_4 + ClO_2 + H_2O$.

Permanganates.—Permanganates evolve Mn_2O_7, a greenish, oily liquid, very explosive on heating.

Fluorides.—To a little CaF_2 in a test-tube add some concentrated H_2SO_4 and warm gently. Introduce into the upper end of the tube a piece of glass tubing carrying a drop of water. This drop will turn turbid owing to the formation of $Si(OH)_4$ as follows:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2;$$

$$2H_2F_2 + SiO_2 \text{ (in the glass of the tube)} \rightarrow SiF_4 \text{ (a gas)} + 2H_2O;$$

$$3SiF_4 + 4H_2O \text{ (on the tube above)} \rightarrow Si(OH)_4 \text{ (a gelatinous precipitate)} + 2H_2SiF_6.$$

Carefully clean and dry the tube and note that it has been etched.

Silicates.—Most natural silicates are affected very little, if at all, by concentrated H_2SO_4. Soluble silicates (*e. g.*, Na_2SiO_3 (water glass) give a gelatinous precipitate of silicic acid.

SPECIAL TESTS.

GROUP I.

Chloride.—Dilute a little NaCl solution and add a few drops of $AgNO_3$ solution. Shake well and note the appearance and color of the precipitate. Test its solubility in HNO_3.

This test for the Cl^- ion is not sufficient unless CN^-, SCN^- and $Fe(CN)_6^{==}$ are known to be absent. If present they must be removed as follows: Acidify the unknown solution with HNO_3 and add $AgNO_3$ solution as long as a precipitate continues to form, heat to boiling, and filter; dry the precipitate, and ignite it to a dull red heat in a *porcelain* crucible. (By this treatment the cyanogen compounds are decomposed with the separation of Ag, while the halides remain unchanged.) Fuse the residue in the same crucible with about 1 gram of pure Na_2CO_3, cool, boil with about 10 cc. of water, and filter. Acidify the solution with HNO_3, and test it with $AgNO_3$.

To several cc. of water in a test-tube add 1 or 2 cc. of CS_2 and a few drops of Cl_2 water. Shake. Does Cl_2 confer any marked color on CS_2?

Bromide.—Dilute a little KBr solution and add a few drops of $AgNO_3$ solution. Shake well and note the color of the precipitate. Test its solubility in HNO_3.

To a dilute solution of KBr add about 1 cc. of CS_2 and a single drop of Cl_2 water and shake. What color is imparted to the CS_2 layer? Note that the color is due to free Br_2, and not to the Br^- ion.

Iodide.—Dissolve a small crystal of KI in about 5 cc. of water, and divide into three portions. To one add $AgNO_3$ solution and shake. Note the color of the precipitate.

To the second portion add CS_2 and a single drop of Cl_2 water and shake. What is the color and what is it due to? Now add a large excess of Cl_2 solution, with vigorous shaking. The mixture now contains HIO_3, which gives no color to CS_2. To the mixture add a little KBr solution. How could you test for Br^- in the presence of I^-?

Acidify the third portion with dilute H_2SO_4, and add CS_2 and KNO_2 solution, shaking vigorously. Note that the I_2 is not oxidized to HIO_3 by an excess of KNO_2. This is the most sensitive test for small amounts of iodide. The equation is: $2KI + 2KNO_2 + 2H_2SO_4 \rightarrow I_2 + 2NO + 2K_2SO_4 + 2H_2O$.

Chlorides, Bromides, and Iodides may be detected in the presence of one another as follows: Dilute the solution largely and use, at first, 1 cc. or less for the tests. Add 5 cc. dil. H_2SO_4 and a few drops of a solution of ferric sulfate. Boil in an 8-inch test-tube, shaking vigorously to prevent bumping. Test the steam which escapes for iodine with starch paper. If iodine is found, boil until it is completely expelled, adding more $Fe_2(SO_4)_3$ from time to time. Add some water and a few drops of $K_2Cr_2O_7$ solution, boil again and test the steam with potassium iodide-starch paper. The bromine, if present, sets iodine free and this turns the paper blue. Care must be taken, however, that the liquid does not touch the paper. Boil till the bromine is completely expelled, adding more $K_2Cr_2O_7$ from time to time, and water, if necessary, to prevent the liquid from becoming too concentrated. Test the solution remaining with $AgNO_3$; a white precipitate is AgCl.

Under the conditions of this test, the $Fe_2(SO_4)_3$ oxidizes only the HI, according to the equation, $Fe_2(SO_4)_3 + 2HI \rightarrow 2FeSO_4 + H_2SO_4 + I_2$; the $K_2Cr_2O_7$ then oxidizes only the HBr, according to the equation, $K_2Cr_2O_7 + 5H_2SO_4 + 6HBr \rightarrow 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2$; and the HCl remains unaltered in the solution.

Cyanide.[1]—To a little KCN (or NaCN) solution in a test-tube add a few drops each of $FeSO_4$ and $Fe_2(SO_4)_3$ solutions. These should produce no precipitate if the solution is acid. (If a blue precipitate is formed, $H_4Fe(CN)_6$ or $H_3Fe(CN)_6$ is present; in that case see Fresenius.) Add NaOH to alkaline reaction, boil for a short time, and then acidify with HCl. Cyanides, if present, are converted into ferrocyanides according to the equation, $FeSO_4 +$

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[1] Owing to the fact that hydrocyanic acid is volatile and a most deadly poison, cyanides should not be given for analysis in an elementary course.

$6KCN \rightarrow K_4Fe(CN)_6 + K_2SO_4$, and, on acidifying, a precipitate of Prussian blue is obtained with the ferric salt present.

Thiocyanate.—To a little NH_4SCN solution add a few drops of $FeCl_3$ solution. A red color, not destroyed by boiling, indicates thiocyanic acid. The color will disappear on adding $HgCl_2$ solution.

Certain organic acids, like acetic acid, give a red color with ferric salts, but, on boiling, a reddish-brown precipitate is formed, and the supernatant liquid is rendered colorless, unless thiocyanic acid is also present.

Ferrocyanide and Ferricyanide.—Add to a little $K_4Fe(CN)_6$ solution a few drops of $FeCl_3$ solution. The dark blue precipitate is $Fe_4(Fe(CN)_6)_3$, called "Prussian blue."

To a little $K_3Fe(CN)_6$ solution add a little $FeSO_4$ solution. The dark blue precipitate is $Fe_3(Fe(CN)_6)_2$, called "Turnbull's blue."

*Ferro*cyanides give with *ferrous* salts (in the absence of air) a white precipitate of $Fe_2^{II}[Fe(CN)_6]^{IV}$. The precipitate obtained is generally light blue, and it rapidly turns darker, owing to oxidation.

*Ferri*cyanides give with *ferric* salts no precipitate, but only a brownish coloration, due to the formation of soluble $Fe^{III}[Fe(CN)_6]^{III}$.

Sulfide.—Dilute a few drops of Na_2S solution in a small beaker with about 15 cc. of water. Acidify with dilute HCl, and cover the beaker with a filter paper which has been moistened with a drop of two of $Pb(C_2H_3O_2)_2$ solution. If necessary, warm the beaker gently.

Sulfides insoluble in dilute acids fail to give this test. Repeat the above experiment using some solid FeS_2 instead of Na_2S solution. Add some pure Zn dust and dilute HCl, and warm. The nascent hydrogen evolved reduces sulfides like FeS_2, HgS, etc., with the evolution of H_2S.

Recall the formation of free sulfur when metallic sulfides are dissolved in HNO_3. Particularly in ores, the separation of the impure sulfur, which tends to float on the surface of the mixture, is strongly indicative of sulfides.

GROUP II.

Nitrite.—Acidify a little KNO_2 solution with HCl or H_2SO_4. The color of the fumes evolved are best seen by looking down through the tube.

Acidify a little $FeSO_4$ solution with 1 or 2 drops of *dilute* H_2SO_4 and add a few drops of KNO_2 solution. The brown color which disappears quickly and does not form in a warm solution, is due to $FeSO_4.NO$, formed as follows:

$$2KNO_2 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_2;$$
$$2FeSO_4 + H_2SO_4 + 2HNO_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O + 2NO;$$
$$FeSO_4 + NO \rightarrow FeSO_4.NO.$$

Nitrate gives the same brown color with $FeSO_4$ in the presence of *concentrated* H_2SO_4. See p. 72.

Solutions of α-naphthylamine and sulfanilic acid, when both are added to an acid solution of a nitrite, give a rose color which develops slowly in very dilute solutions. This reaction is very sensitive (1:1,000,000,000, at least) and is especially suited for water analysis.[1] To about 50 cc. of the water to be tested add 2 cc. of the reagent, stir, and allow to stand 5 or 10 minutes in a tube or beaker covered to exclude the oxides of nitrogen in the air of the laboratory.

Acetate.—To a little $NaC_2H_3O_2$ solution in a test-tube add about 1 cc. of alcohol and 1 or 2 cc. of concentrated H_2SO_4, and warm gently. The odor is that of ethyl acetate, $C_2H_5.C_2H_3O_2$. Write equations, showing the reactions taking place in two steps.

GROUP III.

Sulfite.—Recall the action of strong acids on sulfites. (See Reactions with Concentrated H_2SO_4, p. 64.)

Place a little Na_2SO_3 solution in a test tube fitted with a thistle tube and a delivery tube, add a few cc. of dilute H_2SO_4 and warm, passing the gas evolved into a test-tube containing some dilute NH_4OH. Now add a few drops of $Ba(NO_3)_2$ to the solution of $(NH_4)_2SO_3$ thus obtained. Is $BaSO_3$ soluble in water? in acids?

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[1] The reagent is prepared as follows: Dissolve 0.5 gram sulfanilic acid in 150 cc. dil. $HC_2H_3O_2$; boil 0.2 gram solid α-naphthylamine with 20 cc. water, pour off the colorless solution from the residue (rejecting the latter), and add to the liquid 150 cc. dil. $HC_2H_3O_2$; then mix the two solutions. If the solution becomes reddish in color, shake it with zinc dust, and filter.

Repeat the above experiment, only passing the SO_2 gas into a test-tube containing 5 cc. of water to which has been added a drop or so of $KMnO_4$ solution and about 1 cc. of $BaCl_2$ solution. Write equations for the action of H_2SO_3 on $KMnO_4$ solution, and for a representative product of this reaction on $BaCl_2$ solution.

Test a little of the stock solution of Na_2SO_3 for sulfate. (See Sulfate, p. 74.) The sulfate present is due to the oxidation of the sulfite by the oxygen of the air.

To a little $AgNO_3$ solution add Na_2SO_3 solution. Note that Ag_2SO_3 is stable, and does not darken. (Cf. Thiosulfate, in next procedure.)

Thiosulfate.—Recall the action of strong acids on thiosulfates. (See Reactions with Concentrated H_2SO_4, p. 64.)

Dilute 1 cc. of $Na_2S_2O_3$ solution to a convenient volume, add a single drop of $AgNO_3$ solution, and shake promptly. The precipitate of $Ag_2S_2O_3$ which is first formed dissolves in the excess of $Na_2S_2O_3$, giving a colorless solution which may be assumed to contain $NaAgS_2O_3$. Now add an excess of $AgNO_3$ and warm. The $Ag_2S_2O_3$ is hydrolyzed, forming $Ag_2S + H_2SO_4$. How could these reactions be used to distinguish a thiosulfate from a sulfite? (See Tables, Reactions of Anions, p. 88.)

Carbonate.—Put 2 or 3 cc. of Na_2CO_3 solution in a test-tube fitted with a thistle tube and a delivery tube and slowly add dilute H_2SO_4. Pass the gas evolved into $Ca(OH)_2$ solution in a second test-tube. Two stages may be noted in the $Ca(OH)_2$ reaction. Explain by equations.

Certain natural carbonates, as magnesite and dolomite, react very slowly with acids, and gentle heating may be necessary to start the reaction.

Oxalate.—Place a little $(NH_4)_2C_2O_4$ solution in the test-tube outfit used in the above procedure, and add dilute H_2SO_4 and test for the evolution of CO_2. Repeat, introducing a small amount of MnO_2 before adding the acid. Would this test be dependable in the presence of a carbonate? How may carbonates be removed before making this test? (See Carbonates and Oxalates under Reactions with Concentrated H_2SO_4, p. 65.)

Borate.—Acidify a little $Na_2B_4O_7$ solution with dilute HCl and moisten a piece of turmeric paper with the mixture. Now put the wet paper on the upper side of a watch glass and dry over a beaker of boiling water. Describe the color. Now touch the paper with a stirring rod that has just been dipped in NaOH solution. What is the color?

To 2 or 3 cc. of a concentrated solution of $Na_2B_4O_7$ in an evaporating dish add an equal volume of alcohol and about 2 cc. of concentrated H_2SO_4. Warm gently and set fire to the vapors. Write equations, (1) the action between borate and H_2SO_4, and (2) between one of the products and the alcohol. Ethyl borate, $(C_2H_5)_3BO_3$, is volatile and burns with a green flame, very similar in color to the copper flame. Naturally, the presence of the latter interferes with this test for borates.

Phosphate.—To 2 or 3 cc. of Na_2HPO_4 solution add 5 cc. of $(NH_4)_2MoO_4$ solution (in HNO_3) and warm. The yellow precipitate has the approximate composition $(NH_4)_3PO_4 \cdot 12MoO_3$.

Repeat the experiment, using H_3AsO_4 solution instead of Na_2HPO_4. A very similar precipitate is formed. How may arsenates be removed, so as not to interfere with this test?

Tartrate.—Heat a little dry tartaric acid, $H_2C_4H_4O_6$, or a tartrate in a porcelain crucible. The mass will blacken and give an odor resembling "burnt" sugar.

Make a little $Na_2C_4H_4O_6$ solution slightly alkaline with NH_4OH and add $CaCl_2$ solution in excess. Allow the mixture to stand for a short time. Filter off the precipitate and digest it in the cold with NaOH solution. Dilute the solution slightly, filter and boil the filtrate. The precipitate is white $CaC_4H_4O_6$. The explanation is, $CaC_4H_4O_6$ is soluble in concentrated alkalies in the cold, but is reprecipitated on boiling. Filter hot, wash, introduce the precipitate into a test-tube, add 1 drop of NH_4OH and a little $AgNO_3$ and warm. The tartrate ion will be oxidized by the $AgNO_3$ and the latter will be reduced to metallic silver, which will give a black precipitate, or form a silver mirror on the walls of the tube. (No equation need be written.)

Arsenite and Arsenate.—The presence of these anions is indicated during the metallic analysis in the detection of As in Group II. Trivalent arsenic is present in acid solutions as the cation, As^{+++}, and in alkaline solutions as the arsenite anion, AsO_3^{---}; pentavalent arsenic is always present as arsenate, AsO_4^{---}, regardless of the nature of the solution. Trivalent and pentavalent arsenic may be distinguished in the following way:

Acidify a solution of Na_3AsO_3 with 1 or 2 drops of dilute HNO_3, add a few drops of $AgNO_3$ solution, and by means of a thistle tube introduce this solution beneath some NH_4OH in a test-tube. A yellow precipitate of Ag_3AsO_3 is formed in the neutral zone at the junction of the two liquids. This color zone may be broadened by careful stirring.

Repeat the above experiment using K_3AsO_4 instead of Na_3AsO_3. Reddish-brown Ag_3AsO_4 is precipitated in the neutral zone.

Chromate and Dichromate.—The presence of chromate and dichromate is recognized during the metallic analysis. An orange-colored solution in Group II, which gives a green solution with the separation of sulfur upon saturation with H_2S, followed by the detection of Cr in Group III, indicates chromate or dichromate. Which of these two anions was present in the original substance may be known from its color, chromates being yellow (usually) and dichromates orange.

GROUP IV.

Nitrate.—Add a few drops of $NaNO_3$ solution to 2 or 3 cc. of saturated $FeSO_4$ in a test-tube, and by means of a thistle tube or pipette introduce concentrated H_2SO_4 below the mixture. A brown zone will form at the contact of the two liquids.[1] The brown color is due to a compound of the approximate composition $FeSO_4.NO$. Complete and balance the following equations:

$$NaNO_3 + \text{conc. } H_2SO_4 \rightarrow$$
$$FeSO_4 + HNO_3 + H_2SO_4 \rightarrow NO, \text{ etc.}$$
$$FeSO + NO \rightarrow$$

The brown compound, $FeSO_4.NO$, is easily decomposed by heat; for that reason the liquids must be kept cold during the test.

Chlorates, iodides, and chromates interfere with the test, so that, if present, they must first be removed. To remove chlorates, mix the substance in a porcelain crucible with dry Na_2CO_3 and ignite gently for 5 or 10 minutes. The chlorate is thus changed to chloride; the nitrate is at the same time partially reduced to nitrite, which gives the same reaction with $FeSO_4$ solution. To remove chromates, warm the solution which has been previously acidified with dil. H_2SO_4, with the addition of Na_2SO_3 solution, drop by drop, till the color becomes a pure green. Add NH_4OH, and filter off the $Cr(OH)_3$; test the filtrate with $FeSO_4$ and H_2SO_4. To remove iodides, add to the solution, acidified with dil. H_2SO_4, Ag_2SO_4 solution, as long as a precipitate continues to form, filter, and test the filtrate as described above.

Chlorate.—Recall the reaction of concentrated H_2SO_4 with chlorates. (See Reactions with Concentrated H_2SO_4, p. 65.)

Chlorate in the presence of other anions may be tested for in the following way:

Acidify the solution to be tested with HNO_3, add $AgNO_3$ as long as a precipitate forms, and filter. Make the filtrate alkaline with pure Na_2CO_3, evaporate to dryness, ignite at a low red heat, dissolve in water, and add dil. HNO_3 and $AgNO_3$. This test is very delicate, but it is given by perchlorates as well.

Permanganate.—The presence of the MnO_4^- ion is indicated by the purple color of the original solution, the bleaching out of this color and the possible separation of sulfur upon saturation with H_2S in Group II, and the detection of Mn in Group III of the metallic ions.

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[1] Nitrous acid gives with the slightly acid $FeSO_4$ solution the same dark colored compound, but in this case the brown coloration appears before the mixture is poured into the tube containing the conc. H_2SO_4.

GROUP V.

Sulfate.—To some dilute K_2SO_4 solution add a few drops of $Ba(NO_3)_2$[1] solution. The precipitate is $BaSO_4$, insoluble in HCl or HNO_3.

To 2 or 3 cc. concentrated HNO_3 in a test-tube add some saturated $Ba(NO_3)_2$ solution. The precipitate is $Ba(NO_3)_2$. Explain its formation. How may it be distinguished from $BaSO_4$?

Fluoride.—The drop-of-water test (see Reactions with Concentrated H_2SO_4, p. 65) is used.

GROUP VI.

Silicate.—The only common silicates soluble in water are those of K and Na. If HCl is added drop by drop to a strong solution of a silicate, most of the silicic acid separates in the gelatinous form. If the acid is added quickly, the silicic acid sometimes remains entirely in solution. If the acid solution is evaporated completely to dryness, but with care not to heat the residue after it is dry, on moistening it with conc. HCl (or HNO_3 if Ag is present) and then treating it with hot water, the silicic acid will remain undissolved. The same method serves for the detection and separation of silicic acid in silicates which are decomposed by conc. HCl or HNO_3.

The silica obtained above or the silica in any silicate will dissolve with effervescence in a bead of Na_2CO_3, but both are insoluble in a bead of sodium metaphosphate (obtained from $NaNH_4HPO_4$, "microcosmic salt").

Prepare a metaphosphate bead by making a small loop in a platinum wire, heating, and bringing the hot wire in contact with

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[1] $Ba(NO_3)_2$ is preferred to $BaCl_2$ as a reagent for the SO_4^{--} ion, because the Cl^- ion of the latter solution combines with Pb^{++}, Ag^+ and Hg_2^{++}, completely masking the effect of the Ba^{++}, and leading to wrong inferences. $Ba(NO_3)_2$ is not handicapped by any such limitations.

"microcosmic salt," $NaNH_4HPO_4$. Some of the solid will adhere. Reheat, and keep on adding more solid until, after effervescence has ceased, a clear glassy bead about 2 mm. in diameter is obtained. Complete the equation: $NaNH_4HPO_4 \rightarrow NaPO_3$, etc. Bring the hot bead in contact with a minute amount of finely powdered SiO_2. The SiO_2 will not dissolve, but will remain suspended in the bead—the so-called "silica skeleton."

GROUP VII.

Anions of Organic Acids.—The presence of organic anions, or rather of organic matter in general, can be detected by the carbonization which occurs when the substance is heated in a closed tube. The number of the organic acids is so great that any systematic scheme of analysis for all of these anions is impossible. Practically, the examination for such anions resolves itself into special tests for those which are suspected to be present in a given case.

Many organic acids are precipitated on adding an acid to solutions of their salts. Such acids can often be identified by their melting-points, determined with the dry acid in a capillary tube. Many acids may also be extracted from aqueous HCl solutions by means of ether and are left as a liquid or solid residue when the solvent is evaporated. On distilling aqueous solutions, many acids, especially monobasic ones, pass over with the water vapor. It seems scarcely desirable to select particular acids for further discussion.

THE ANIONS.

ANALYSIS.

(29.) General Procedure.

(a) Carry out the regular analysis for the metallic ions. Watch for evidence of the following anions, the metals of which will be found during the metallic analysis: Arsenite, arsenate, permanganate, chromate and dichromate.

(b) Try the effect of concentrated H_2SO_4 on a portion of the solid (or better, moistened with a drop of water) substance in a test-tube. In case of a solution, evaporate nearly to dryness, transfer to a test-tube, and then add the concentrated H_2SO_4. Interpret very carefully the resultant effects.

(c) In case the substance is a solid, find whether it is soluble in water or in strong acids; if it is a solution, test it with litmus paper. A lavender color indicates approximate neutrality, while a pink-red indicates free acids and a blue free bases. The approximately neutral solutions, of course, can contain only water-soluble salts.

(d) From the solubility table (inside back cover) infer what anions might be present with the cations already found under the solubility conditions found in the preceding paragraph.

(e) Classify the substance under one of the following cases, and follow the procedure indicated.

Case I.—The substance is a solid soluble in water (or such a solution) and contains no cations other than Na^+, K^+, NH_4^+, H^+.

Infer from the results of the reaction with concentrated H_2SO_4 (see (b) above) if the anions of any of the volatile or unstable acids (*i. e.*, H_2S, HNO_2, H_2CO_3, H_2SO_3, $H_2S_2O_3$) are present. Make tests on portions of the original substance for such anions as may be indicated.

Test separate portions of the solution for the anions of Group I by (**30.**), Group V by (**31.**), and Group III by (**33.**) and (**34.**).

Test separate portions of the solution for the members of Groups II and IV.

Case II.—The substance is soluble in water, but contains cations other than Na^+, K^+, NH_4^+ and H^+. Use Procedure A or Procedure B.

Procedure A.—Infer from the solubility table (see inside back cover) what anions could be present in a water solution containing the cations found in the metallic analysis.[1] Test for these ions on separate portions of the unknown substance without attempting to ascertain the anion groups present.

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[1] A number of salts listed in the solubility table as "soluble" may give turbid solutions, owing to the formation of insoluble salts, either by hydrolysis or by reaction with gases dissolved in the water, like CO_2. *E. g.*, $Hg_2(NO_3)_2$ gives insoluble $Hg_2(OH)NO_3$, $Pb(C_2H_3O_2)_2$ gives insoluble $Pb(OH_2) . 2 PbCO_3$ (due to CO_2 in the water), $SnCl_4$ gives insoluble $Sn(OH_4)$, $FeCl_3$ gives insoluble $Fe(OH)Cl_2$ (upon boiling), $Al_2(SO_4)_3$ may give insoluble $Al(OH)SO_4$, etc.

Procedure B.—Test separate portions of the solution for Group I by (**30.**)[1] and for Group V by (**31.**).

Remove the "heavy metals" from another portion by (**32.**) and test for Group III by (**33.**) and (**34.**).

Test separate portions of the original for members of Groups II and IV.

Case III.—The substance is a solid insoluble in water, but soluble in strong acids; or an acid solution which forms a precipitate upon neutralization with NaOH or NH_4OH.

A. The substance is in the form of a strongly acid solution.

What anions may be presumed to be absent in all strongly acid solutions?

Test a portion of the solution for Group I anions by (**30.**), and another portion for Group V anions by (**31.**).

Test separate portions of the solutions for members of Groups II and IV.

Remove the "heavy metals" from another portion by (**32.**) and test for Group III by (**33.**) and (**34.**).

If the presence of any of these groups is indicated, test for the members of such groups, using in each case small portions of the original.

B. The substance is (presumably) a mixture of solids, soluble in strong acids.

Dissolve in dilute HNO_3 (or other acid), watching for evidence of the presence of the anions of the unstable acids, and test as in A above.

(**30.**) **Group I.**—Acidify a small portion of the solution with dilute HNO_3, add $AgNO_3$ solution in excess, shake and filter. A precipitate indicates Group I. (The anion is more or less definitely shown by the color of the Ag-precipitate: AgCl, AgCN, $Ag_4Fe(CN)_6$

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[1] The Group I test is made on the original solution instead of the one from which the "heavy metals" have been removed, because the Na_2CO_3 reagent is usually made by the Solvay process and contains NaCl, which would vitiate the test for Group I.

and AgSCN are white, AgBr yellowish-white, AgI yellow, $Ag_3Fe(CN)_6$ orange, Ag_2S brown-black.) Filter and treat the solution according to (**33.**). If the presence of Group I is indicated, test separate portions of the original substance for the several ions of the group.

(**31.**) **Group V.**—Acidify a portion of the solution with dilute HNO_3, dilute with several cc. of water and add $Ba(NO_3)_2$ solution in excess. A precipitate indicates the presence of Group V (sulfate or fluoride). Filter and treat filtrate by (**34**).

(**32.**) **Removal of the Heavy Metals.**—To a portion of the solution add excess of Na_2CO_3 solution and boil. Filter into a beaker, and reject the precipitate. Neutralize the filtrate with dilute HNO_3 and divide into two parts.

To the first portion add $AgNO_3$ solution in excess, shake and filter. Test the filtrate for Group III by (**33.**).

To the second portion add $Ba(NO_3)_2$ solution in excess and filter. Test the filtrate for Group III by (**34.**).

If the presence of Group III is indicated, carry out the special tests for the members of this group on small portions of the original.

(**33.**) **Group III.**—By means of a thistle tube introduce the filtrate from (**30.**) or (**32.**) below 3 or 4 cc. of NH_4OH solution in a test-tube. A white or colored zone between the ammoniacal and acid layers indicates the presence of Groups II or III. Sometimes brown Ag_2O appears, but it soon dissolves in the excess NH_4OH. The identity of the anions is suggested by the color of the zone. $AgC_2H_3O_2$, $AgNO_2$, Ag_2SO_4, Ag_2CO_3, $Ag_2C_2O_4$ and $AgBO_2$[1] are white; Ag_3PO_4 and Ag_3AsO_3 yellow; Ag_3AsO_4 chocolate brown; and Ag_2CrO_4 red. White $Ag_2S_2O_3$ may form momentarily, rapidly going over into black Ag_2S.

(**34.**) Make the filtrate from (**31.**) or (**32.**) alkaline with freshly prepared CO_3-free NaOH solution.[2] A precipitate indicates Group III.

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[1] $AgBO_2$ is not precipitated in (**33.**) by NH_4OH in case the borate was present as the free acid. It must be tested for separately.

[2] Prepared by adding 5 to 10 drops of $Ba(NO_3)_2$ solution to 10 cc. of ordinary NaOH solution and filtering.

If the presence of Groups II and III is indicated, test separate portions of the original substance for the ions of these groups.

Oxides and Hydroxides.—There is no specific test for oxides and hydroxides. In case the tests for the other anions are negative, the substance may be suspected of being an oxide or a hydroxide. Such an inference should be substantiated by comparing the properties of the unknown substance with those of the oxide or hydroxide in question as described in the text-books.

Hydroxides (except NaOH and KOH) may be distinguished from oxides by the fact that they give off water on ignition in a hard glass test-tube.

REACTIONS OF THE METALLIC IONS.

Group I.

Reagent.	Silver. $AgNO_3$.	Mercury (ous). $Hg_2(NO_3)_2$.	Lead. $Pb(NO_3)_2$.
Hydrochloric Acid. HCl.	Silver Chloride. $AgCl$. White pr., insol. in acids, soluble in NH_4OH, in KCN, in $Na_2S_2O_3$. Darkens in the light.	Mercurous Chloride. Hg_2Cl_2. White pr. Sol in. HNO_3, in aqua regia. Converted to $NH_2HgCl + Hg$ by NH_4OH.	Lead Chloride. $PbCl_2$. White pr., slightly soluble in cold water, more easily in hot water. Converted to an insoluble basic salt by NH_4OH.
Hydrogen Sulfide. H_2S.	Silver Sulfide. Ag_2S. Black pr., insol. in $(NH_4)_2S$. Sol. in hot HNO_3.	Mercuric Sulfide and Mercury. $HgS + Hg$. Black pr., partly sol. in HNO_3. Sol. in aqua regia.	Lead Sulfide. PbS. Black pr., insol. in $(NH_4)_2S$. Sol. in HNO_3.
Sulfuric Acid. H_2SO_4.	Silver Sulfate. Ag_2SO_4. White precip., only in concentrated solutions.	Mercurous Sulfate. Hg_2SO_4. White pr., slightly sol. in water.	Lead Sulfate. $PbSO_4$. White pr., insol. in excess, slightly sol. in HNO_3. Soluble in $NH_4C_2H_3O_2$.
Sodium Hydroxide. $NaOH$.	Silver Oxide. Ag_2O. Brown pr., sol. in HNO_3, in NH_4OH.	Mercurous Oxide. Hg_2O. Black pr., soluble in HNO_3, insol. in NH_4OH.	Lead Hydroxide. $Pb(OH)_2$. White pr. Sol. in excess, in HNO_3, insol. in NH_4OH.
Ammonium Hydroxide. NH_4OH.	Silver Oxide. Ag_2O. Brown precip., soluble in excess.	Ammonobasic Mercuric Salt and Mercury. Black precip., insol. in excess.	Basic Salt. White pr., insol. in excess.
Sodium Carbonate. Na_2CO_3.	Silver Carbonate. Ag_2CO_3. White precip., soluble in NH_4OH.	Basic Salt. Yellow pr., quickly becoming black.	Basic Lead Carbonate. $2PbCO_3.Pb(OH)_2$. White pr., "White Lead."
Potassium Chromate. K_2CrO_4.	Silver Chromate. Ag_2CrO_4. Dark red precip., soluble in HNO_3, in NH_4OH.	Mercurous Chromate. Hg_2CrO_4. Dark red pr.	Lead Chromate. $PbCrO_4$. Yellow pr. Slightly sol. in HNO_3. Sol. in NaOH.
Potassium Ferrocyanide. $K_4Fe(CN)_6$.	Silver Ferrocyanide. $Ag_4Fe(CN)_6$. White precip., insoluble in NH_4OH.	Mercurous Ferrocyanide. $Hg_4Fe(CN)_6$. White precipitate.	Lead Ferrocyanide. $Pb_2Fe(CN)_6$. White precipitate.
Stannous Chloride. $SnCl_2$.	Silver Chloride. $AgCl$. White precip.	Mercury. Hg. Dark gray precip.	Lead Chloride. $PbCl_2$. White precipitate.

Group II—A. The Copper Group.

Reagent.	Mercury (ic). $HgCl_2$	Copper. $CuSO_4$.	Bismuth. $BiCl_3$.	Cadmium. $CdSO_4$.
Hydrogen Sulfide. H_2S.	Mercuric Sulfide. HgS. First white, then yellow, reddish brown and black pr., insol. in HNO_3, in $(NH_4)_2S$. Sol. in aq. regia, in $Na_2S + NaOH$	Copper Sulfide. CuS. Black pr., sol. in HNO_3, in KCN. Very slightly sol. in $(NH_4)_2S_x$. Insol. in hot dil. H_2SO_4.	Bismuth Sulfide. Bi_2S_3. Dark brown pr. sol. in HNO_3, insol. in $(NH_4)_2S$.	Cadmium Sulfide. CdS. Yellow pr. sol. in HNO_3, in hot diluted H_2SO , insol. in $(NH_4)_2S$.
Sulfuric Acid. H_2SO_4.	No precipitate.	No precipitate.	No precipitate.	No precipitate.
Ammonium Hydroxide. NH_4OH.	Ammonobasic Mercuric Chloride. $HgNH_2Cl$. White precip.	Basic Copper salt. Greenish-blue pr. sol. in excess to a blue solution.	Bismuthyl Hydroxide. $BiO\ OH$. White pr., insol. in excess.	Cadmium Hydroxide. $Cd(OH)_2$. White precip., sol. in excess.
Sodium Hydroxide. $NaOH$.	Mercuric Oxide. HgO. Yellow pr. In presence of NH_4Cl, white pr. of $HgNH_2Cl$.	Copper Hydroxide. $Cu(OH)_2$. Blue pr. changed to black CuO by boiling.	Bismuthyl Hydroxide. $BiO\ OH$. White precip.	Cadmium Hydroxide. $Cd(OH)_2$. White precip.
Sodium Carbonate. Na_2CO_3.	Mercuric Oxychloride. $HgCl_2 + nHgO$. Reddish br. pr., changed to yellow HgO by boiling.	Basic Copper Carbonate. Blue pr. changed to black CuO by boiling.	Bismuthyl Carbonate. $(BiO)_2CO_3$. White precip.	Cadmium Carbonate. $CdCO_3$. White precip.
Potassium Chromate. K_2CrO_4.	Mercuric Chromate. $HgCrO_4$. Reddish-yellow pr., soluble in HNO_3.	Copper Chromate. $CuCrO_4$. Reddish-brown precip., sol. in NH_4OH to a green solution.	Bismuthyl Dichromate. $(BiO)_2Cr_2O_7$. Yellow pr. sol. in $HC_2H_3O_2$.	———
Potassium Ferrocyanide $K_4Fe(CN)_6$	———	Copper Ferrocyanide. $Cu_2Fe(CN)_6$. Reddish-brown pr. slightly sol. in NH_4OH, insol. in $HC_2H_3O_2$.	Bismuth Ferrocyanide. White pr. insol. in HCl.	Cadmium Ferrocyanide. $Cd_2Fe(CN)_6$. Yellowish-white precip., sol. in HCl.
√ Stannous Chloride. $SnCl_2$.	Mercurous Chloride. Hg_2Cl_2. White pr. An excess of $SnCl_2$ gives gray Hg.	Cuprous Chloride. Cu_2Cl_2. White precip., only in conc. solutions.	Darkens a pr. of Bi O O H, changing it to Bi.	———
Water. H_2O.	———	———	Basic Bismuth Salt. $BiOCl$. White pr., sol. in HCl.	———

Group II—

Reagent.	Arsenic.		Antimony.	
	Arsenious Salts. K_3AsO_3.	Arsenic Salts. KH_2AsO_4.	Antimonious Salts. $SbCl_3$.	Antimonic Salts. $KSbO_3$.
Hydrogen Sulfide. H_2S.	Arsenic trisulfide. As_2S_3. Yellow pr., sol. in alkalies and alkali sulfides. Insol. in conc. HCl. Sol. in $(NH_4)_2CO_3$, reprecipitated by acids.	Arsenic trisulfide and sulphur. $As_2S_3 + 2S$. Yellow precip. forming slowly and on warming. Sol. in $(NH_4)_2CO_3$, reprecipitated by acids.	Antimony trisulfide. Sb_2S_3. Orange pr. sol. in conc. HCl, in alkalies and alkali sulfides. Almost insol. in $(NH_4)_2CO_3$.	Antimony pentasulfide. Sb_2S_5. Orange pr. sol. in conc. HCl, in alkalies and alkali sulfides. Almost insol. in $(NH_4)_2CO_3$.
Ammonium Sulphide. $(NH_4)_2S$.	Arsenic trisulfide. As_2S_3. Only in acid solutions. Sol. in excess.	Arsenic pentasulfide. As_2S_5. Only in acid solutions. Sol. in excess.	Antimony trisulfide. Sb_2S_3. Sol. in excess.	Antimony pentasulfide. Sb_2S_5. Sol. in excess.
Sodium Hydroxide. NaOH.	——	——	Antimonious Hydroxide. $Sb(OH)_3$. White pr., sol. in excess.	Sodium Metantimonate. $NaSbO_3$. White pr. sol. in excess.
Potassium Hydroxide. KOH.	——	——	Antimonious Hydroxide. $Sb(OH)_3$.	——
Ammonium Hydroxide. NH_4OH.	——	——	Antimonious Hydroxide. $Sb(OH)_3$. Insol. in excess.	Ammonium Metantimonate. NH_4SbO_3. Nearly insol. in excess.
Sodium Carbonate. Na_2CO_3.	——	——	Antimonious Hydroxide. $Sb(OH)_3$. Sol. in excess on boiling.	——
Silver Nitrate. $AgNO_3$.	Silver Arsenite. Ag_3AsO_3. Yellow pr., sol. in HNO_3, in NH_4OH.	Silver Arsenate. Ag_3AsO_4. Reddish-brown pr., sol. in HNO_3, in NH_4OH.	Silver Chloride and Antimony trioxide. $AgCl + Sb_2O_3$. White precip.	Silver Antimonate. $AgSbO_3$. White pr., sol. in NH_4OH.
Mercuric Chloride. $HgCl_2$.	Mercuric Arsenite. $Hg_3(AsO_3)_2$ White pr., sol. in acids.	——	Antimony Oxychloride. Caused by dilution. Sol. in conc. HCl.	——
Stannous and Stannic Chlorides. $SnCl_2 + SnCl_4$.	——	——	——	——
Magnesia Mixture. NH_4Cl, NH_4OH, $MgCl_2$	——	Magnesium Ammonium Arsenate. $MgNH_4AsO_4$. White crys. pr., sol. in $C_2H_4O_2$.	Same pr. as by NH_4OH.	Same precip. as by NH_4OH.
Metallic Zinc and Hydrochloric Acid. (Marsh's test.)	Hydrogen and Hydrogen Arsenide. The flame deposits a spot on porcelain. Sol. in sodium hypochlorite. Sol. in $(NH_4)_2S$; on evaporation the yellow residue is insol. in conc. HCl.		Hydrogen and Hydrogen Antimonide. The flame deposits a spot on porcelain. Insol. in sodium hypochlorite. Sol. in $(NH_4)_2S$. On evaporation the orange residue is sol. in conc. HCl.	

B. The Tin Group.

Tin.		Platinum.	Gold.
Stannous Salts. $SnCl_2$.	Stannic Salts. $SnCl_4$.	H_2PtCl_6.	$HAuCl_4$.
Stannous Sulfide. SnS. Dark brown pr., sol. in conc. HCl in alkalies. Difficultly sol. in yellow $(NH_4)_2S$. Insol. in $(NH_4)_2CO_3$.	Stannic Sulfide. SnS_2. Yellow pr., sol. in conc. HCl, in alkalies and alkali sulfides, in alkali carbonates. Insol. in $(NH_4)_2CO_3$.	Platinic Sulfide. PtS_2. Dark brown pr., insol. in conc. HCl. Difficultly sol. in alkali sulphides. Sol. in aqua regia.	Gold Sulfide. Au_2S_3. Black pr., insol. in conc. HCl. Sol. in alkali sulfides, sol. in aqua regia.
Stannous Sulfide. SnS. Sol. in yellow $(NH_4)_2S$.	Stannic Sulfide. SnS_2. Sol. in excess.	Platinic Sulfide. PtS_2. Sol. in excess.	Gold Sulfide. Au_2S_3. Sol. in excess.
Stannous Hydroxide. $Sn(OH)_2$. White pr., sol. in excess.	Stannic Hydroxide. $Sn(OH)_4$. White pr., sol. in excess.	—	—
Stannous Hydroxide. $Sn(OH)_2$.	Stannic Hydroxide. $Sn(OH)_4$.	Potassium Chloroplatinate. K_2PtCl_6. Yellow pr. in presence of free HCl.	—
Stannous Hydroxide. $Sn(OH)_2$. Insol. in excess. Darkens on boiling.	Stannic Hydroxide. $Sn(OH)_4$. Slightly sol. in excess.	Ammonium Chloroplatinate. $(NH_4)_2PtCl_6$. Yellow pr., sol. in great excess.	Fulminating Gold $\left[Au\begin{matrix}(NH_3)_2\\(OH)_2\end{matrix}\right]OH$. Yellow pr., insol. in excess.
Stannous Hydroxide. $Sn(OH)_2$. Insol. in excess.	Stannic Hydroxide. $Sn(OH_4)$. Slightly sol. in excess.	—	—
Silver Chloride and Silver. $AgCl + Ag$.	Silver Chloride. $AgCl$.	Silver Chloride and Platinum Oxide. $AgCl + PtO_2$. Brown precipitate.	Silver Chloride and Gold Oxide. $AgCl + Au_2O_3$. Brown precipitate.
Mercurous Chloride. Hg_2Cl_2. White pr., insol. in cold conc. HCl.	—	—	—
—	—	—	Purple of Cassius. Purple red precip. or coloration.
Same precip. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.
Metallic Tin.	In neutral solution, also Stannic Hydroxide.	Platinum. Black precipitate.	Gold. Brown precipitate.

Group

Reagent.	Aluminium. $KAl(SO_4)_2$.	Chromium. $KCr(SO_4)_2$.	Zinc. $ZnCl_2$.	Manganese. $MnCl_2$.
Ammonium Sulfide. $(NH_4)_2S$.	Aluminium Hydroxide. $Al(OH)_3$. White flocculent pr.	Chromium Hydroxide. $Cr(OH)_3$. Grayish-green pr.	Zinc Sulfide. ZnS. White pr. insol. in $C_2H_4O_2$. Sol. in HCl.	Manganese Sulfide. MnS. Flesh col'd pr. sol. in HCl, in $C_2H_4O_2$. Oxidizes in the air.
Hydrogen Sulfide. H_2S.	—	—	Zinc Sulfide. Only in neutral alkaline acid or acetic acid solution.	Manganese Sulfide. Only in neutral or alkaline solutions.
Ammonium Hydroxide. NH_4OH.	Aluminium Hydroxide. $Al(OH)_3$. White flocculent pt. very slightly sol. in excess.	Chromium Hydroxide. $Cr(OH)_3$. Grayish-blue or green precip. slightly sol. in excess with a red color.	Zinc Hydroxide, $Zn(OH)_2$. White pr. sol. in excess. In presence of NH_4Cl no pr.	Manganese Hydroxide. $Mn(OH)_2$. White pr. becoming brown. In presence of NH_4Cl a dark brown pr. forms slowly by oxidation.
Sodium Hydroxide. NaOH.	Aluminium Hydroxide. $Al(OH)_3$. White pr. sol. in excess as $NaAlO_2$.	Chromium Hydroxide. $Cr(OH)_3$. Sol. in excess to a green sol. Reprecipitated by boiling.	Zinc Hydroxide $Zn(OH)_2$. White pr. sol. in excess. Reprecipitated by boiling.	Manganese Hydroxide. $Mn(OH)_2$. White pr. becoming brown. Insol. in excess.
Barium Carbonate. $BaCO_3$.	Aluminium Hydroxide. $Al(OH)_3$. White pr.	Basic Salt. Greenish pr.	No pr. in the cold except in presence of a sulfate.	No pr. in the cold except in presence of a sulfate.
Sodium Phosphate. Na_2HPO_4.	Aluminium Phosphate. $AlPO_4$. White pr. sol. in NaOH, insol. in $C_2H_4O_2$.	Chromium Phosphate. $CrPO_4$. Green pr.	Zinc Phosphate $Zn_3(PO_4)_2$. White pr. sol. in excess.	Manganese Phosphate. $Mn_3(PO_4)_2$. White pr. sol. in NH_4OH.
Potassium Ferrocyanide. $K_4Fe(CN)_6$.	White pr. forms slowly.	—	Zinc Ferrocyanide. $Zn_2Fe(CN)_6$. White pr. sol. in HCl.	Manganese Ferrocyanide. $Mn_2Fe(CN)_6$. Reddish-white precip. sol. in HCl.
Potassium Ferricyanide. $K_3Fe(CN)_6$.	—	—	Zinc Ferricyanide. $Zn_3[Fe(CN)_6]_2$. Yellowish-brown pr. sol. in HCl.	Manganese Ferricyanide. $Mn_3[Fe(CN)_6]_2$. Brown pr. insol. in HCl.
Ammonium Thiocyanate. NH_4SCN.	—	—	—	—
Dimethylglyoxime	—	—	—	—
Borax bead.	—	Yellowish-green, hot. Emerald green, cold.	—	Violet red, hot. Amethyst red, cold. Colorless in R. F.

III.

Ferric Salts. $FeCl_3$.	Ferrous Salts. $FeCl_2$.	Cobalt. $CoCl_2$.	Nickel. $NiCl_2$.	Uranium. $UO_2(NO_3)_2$.
Iron Sulfide. Fe_2S_3. Black pr. sol. in acids to a ferrous salt.	Iron Sulfide. FeS. Black pr. sol. in HCl, in $C_2H_4O_2$. Oxidizes in the air.	Cobalt Sulfide. CoS. Black pr. insol. in $C_2H_4O_2$, very slowly sol. in HCl. Sol. in aq. reg.	Nickel Sulfide. NiS. Black pr. slightly sol. in exc. very slowly sol. in HCl. Sol. in aq. reg.	Uranyl Sulfide. UO_2S. Dk. br. pr. somewhat sol. in exc. of colorless $(NH_4)_2S$.
Reduced to a ferrous salt with separation of sulfur.	No pr. in acid solution.	Cobalt Sulfide. Only in neutral or alkaline solutions.	Nickel Sulfide. Only in neutral or alkaline solutions.	———
Ferric Hydroxide. $Fe(OH)_3$. Reddish-brown pr. insol. in excess.	Ferrous Hydroxide. $Fe(OH)_2$. White pr. becoming green and reddish-brown. In presence of NH_4Cl, $Fe(OH)_3$ forms slowly.	Basic Salt. Blue pr. sol. in excess to a red sol. In presence of NH_4Cl, no pr.	Nickel Hydroxide. $Ni(OH)_2$. Green pr. sol. in excess to a blue sol. In presence of NH_4Cl no pr.	Ammonium Uranate. $(NH_4)_2U_2O_7$. Yellow pr.
Ferric Hydroxide. $Fe(OH)_3$. Reddish-brown pr. insol. in excess.	Ferrous Hydroxide. $Fe(OH)_2$. White pr. becoming green and reddish brown, insol. in excess.	Basic Salt. Blue pr. insol. in excess. Sol. in $C_2H_4O_2$, in NH_4OH.	Nickel Hydroxide. $Ni(OH)_2$. Apple green pr. insol. in excess, sol. $C_2H_4O_2$, in NH_4OH.	Sodium Uranate. $Na_2U_2O_6$. Yellow pr. sol. in $(NH_4)_2CO_3$.
Basic Salt. Reddish-brown pr.	No. pr. in the cold except in the presence of a sulfate.	No. pr. in the cold except in presence of a sulfate.	No pr. in the cold except in presence of a sulfate.	Uranyl Hydroxide. $UO_2(OH)_2$. Yellow pr.
Ferric Phosphate. $FePO_4$. Yellowish-white pr. sol. in excess. Insol. in $C_2H_4O_2$.	Ferrous Phosphate. $Fe_3(PO_4)_2$. White pr. becoming blue in the air.	Cobalt Phosphate. $Co_3(PO_4)_2$. Red pr. sol. in NH_4OH.	Nickel Phosphate. $Ni_3(PO_4)_2$. Green pr. sol. in NH_4OH.	Uranyl Phosphate. UO_2HPO_4. Yellowish-white pr.
Ferric Ferrocyanide. $Fe_4[Fe(CN)_6]_3$. Dark blue pr. insol. in HCl. Decomposed by NaOH.	Ferrous Ferrocyanide. $Fe_2Fe(CN)_6$. Bluish-white pr. becoming blue.	Cobalt Ferrocyanide. $Co_2Fe(CN)_6$. Green pr. becoming greenish-blue, insol. in HCl.	Nickel Ferrocyanide. $Ni_2Fe(CN)_6$. Greenish-white pr. insol. in HCl.	Uranyl Ferrocyanide $(UO_2)_2[Fe(CN)_6]$. Reddish-brown pr.
Reddish-brown color.	Ferrous Ferricyanide. $Fe_3[Fe(CN)_6]_2$. Dark blue pr. insol. in HCl. Decomposed by NaOH.	Cobalt Ferricyanide. $Co_3[Fe(CN)_6]_2$. Dark brown pr. insol. in HCl.	Nickel Ferricyanide. $Ni_3[Fe(CN)_6]_2$. Yellowish-green pr. insol. in HCl.	———
Blood red solution. $Fe(SCN)_3$. Most delicate with HCl.	No color.	———	———	Red color.
———	———	Brown Solution.	Nickel Dimethylglyoxime $Ni(C_2N_2H_3O_2)_2$. Red precipitate, soluble in strong acids.	———
Yellow in O. F. Green in R. F.	Yellow in O. F. Green in R. F.	Blue.	Violet, hot. Reddish-brown, cold, gray and turbid in R. F.	Yellow in O. F. Green in R. F.

Group IV.

Reagent.	Barium. $BaCl_2$.	Strontium. $SrCl_2$.	Calcium. $CaCl_2$.	Magnesium. $MgSO_4$.
Ammonium Carbonate. $(NH_4)_2CO_3$.	Barium Carbonate. $BaCO_3$. White pr. sol. in acids.	Strontium Carbonate. $SrCO_3$. White pr. sol. in acids.	Calcium Carbonate. $CaCO_3$. White pr. sol. in acids.	Basic Magnesium Carbonate. $MgCO_3 + nMg(OH)_2$. White pr. on warming and in absence of NH_4 salts.
Sodium Hydroxide. NaOH.	Barium Hydroxide. $Ba(OH)_2$. White pr. only in conc. solutions.	Strontium Hydroxide. $Sr(OH)_2$. White pr. difficultly sol. in water.	Calcium Hydroxide. $Ca(OH)_2$. White pr. difficultly sol. in water.	Magnesium Hydroxide. $Mg(OH)_2$. White pr. sol. in NH_4Cl.
Ammonium Hydroxide. NH_4OH.	No pr.	No pr.	No pr.	Magnesium Hydroxide. $Mg(OH)_2$. Sol. in NH_4Cl.
Ammonium Sulfate. $(NH_4)_2SO_4$.	Barium Sulfate. $BaSO_4$. White pr. insol. in water or in acids.	Strontium Sulfate. $SrSO_4$. White pr. very little sol. in water or in $(NH_4)_2SO_4$.	Calcium Sulfate. $CaSO_4$. White pr. somewhat sol. in water. Insol. in alcohol.	——
Ammonium Oxalate. $(NH_4)_2C_2O_4$.	Barium Oxalate. BaC_2O_4. White pr. sol. in HCl, slightly sol. in $C_2H_4O_2$.	Strontium Oxalate. SrC_2O_4. White pr. sol. in HCl, slightly sol. in $C_2H_4O_2$.	Calcium Oxalate. CaC_2O_4. White pr. sol. in HCl, almost insol. in $C_2H_4O_2$ or $H_2C_2O_4$.	No precipitate in dilute solutions.
Potassium Dichromate. $K_2Cr_2O_7$.	Barium Chromate. $BaCrO_4$. Yellow pr. insol. in $C_2H_4O_2$ in presence of $K_2Cr_2O_7$. Sol. in HCl.	Strontium Chromate. $SrCrO_4$. Yellow pr. sol. in $C_2H_4O_2$.	Calcium Chromate. $CaCrO_4$. Yellow pr. sol. in $C_2H_4O_2$.	——
Sat. Calcium Sulfate. $CaSO_4$.	Barium Sulfate. $BaSO_4$. White pr. forms immediately.	Strontium Sulfate. $SrSO_4$. White pr. forms slowly.	——	——
Sodium Phosphate. Na_2HPO_4.	Barium Hydrogen Phosphate. $BaHPO_4$. White pr. sol. in acids.	Strontium Hydrogen Phosphate. $SrHPO_4$. White pr. sol. in acids.	Calcium Hydrogen Phosphate. $CaHPO_4$. White pr. sol. in acids.	Magnesium Hydrogen Phosphate. $MgHPO_4$. White pr. in presence of NH_4OH and NH_4Cl a white cryst. pr. of $MgNH_4PO_4$ is formed. Sol. in $C_2H_4O_2$.
Flame.	Yellowish-green.	Bright red.	Yellowish-red.	——

Group V.

Reagent.	Lithium. LiCl.	Ammonium. NH_4Cl.	Sodium. NaCl.	Potassium. KCl.
Sodium Carbonate. Na_2CO_3.	Lithium Carbonate. Li_2CO_3. White pr. slightly sol. in water.	Ammonia. NH_3. On boiling.	—	—
Sodium Phosphate. Na_2HPO_4.	Lithium Phosphate. Li_3PO_4. White pr. slightly sol. in H_2O. Sol. in HCl.	—	—	—
Chloro-platinic Acid. H_2PtCl_6.	—	Ammonium Chloroplatinate. $(NH_4)_2PtCl_6$. Yellow pr. slightly sol. in water. Insol. in alcohol.	—	Potassium Chloroplatinate. K_2PtCl_6. Yellow precip. slightly sol. in water, insol. in alcohol.
Perchloric acid. $HClO_4$.	—	—	—	White cryst. precip. $KClO_4$. Slightly sol. in water.
Tartaric Acid. $H_2C_4H_4O_6$.	—	Mono-Ammonium Tartrate. $NH_4HC_4H_4O_6$. White cryst. pr. on shaking. Slightly sol. in water.	—	Mono-Potassium Tartrate. $KHC_4H_4O_6$. White cryst. pr. on shaking and rubbing. Somewhat sol. in water.
Potassium Pyroantimonate. $K_2H_2Sb_2O_7$.	—	—	Sodium Pyroantimonate. $Na_2H_2Sb_2O_7$. White cryst. pr., best in slightly alkaline solutions.	—
Nessler's Reagent. $K_2HgI_4 +$ KOH.	—	Reddish-brown pr. or yellow color, very delicate.	—	—
Sodium Hydroxide. NaOH.	—	Evolves NH_3 on warming.	—	—
Hydrofluosilicic Acid. H_2SiF_6.	—	—	Sodium Fluosilicate. Na_2SiF_6. White pr. somewhat sol. in water, insol. in 50% alcohol.	Potassium Fluosilicate. K_2SiF_6. Transparent pr. slightly sol. in H_2O.
Flame.	Red.	—	Yellow.	Violet.

REACTIONS OF

I.—Inorganic

Salts of	Barium Chloride.	Calcium Chloride.	Silver Nitrate.
Sulfuric Acid. H_2SO_4.	White pr. insol. in acids.	White pr. somewhat sol. in water and in acids.	White pr. only in conc. solutions.
Hydrofluosilicic Acid. H_2SiF_6.	White pr. insol. in HCl.	———	———
Sulfurous Acid. H_2SO_3.	White pr. sol. in HCl.	White pr. sol. in HCl.	White pr. decomposed by boiling into Ag, Ag_2SO_4 and SO_2.
Thiosulfuric Acid. (Hyposulfurous.) $H_2S_2O_3$.	White pr. only in conc. solutions.	———	White pr. sol. in $Na_2S_2O_3$. Decomposes into H_2SO_4 and black Ag_2S.
Phosphoric Acid. H_3PO_4.	White pr. sol. in acids.	White pr. sol. in acids, even in $HC_2H_3O_2$.	Yellow pr. sol. in HNO_3, in NH_4OH.
Pyrophosphoric Acid. $H_4P_2O_7$.	White pr. sol. in HCl.	White pr. sol. in an excess of the pyrophosphate.	White pr. sol. in HNO_3, NH_4OH.
Metaphosphoric Acid. HPO_3.	White pr. sol. in excess of the metaphosphate.	White pr.	White pr. sol. in HNO_3, in NH_4OH.
Arsenic Acid. H_3AsO_4.	White pr. sol. in acids.	White pr. sol. in $HC_2H_3O_2$.	Reddish-brown pr. sol. in HNO_3, in NH_4OH.
Arsenious Acid. H_3AsO_3.	White pr. sol. in acids.	White pr. sol. in $HC_2H_3O_2$.	Yellow pr. sol. in HNO_3, in NH_4OH.
Chromic Acid. H_2CrO_4.	Yellow pr. sol. in HCl, in HNO_3, insol. in $HC_2H_3O_2$.	———	Dark red pr. sol. in HNO_3.
Boric Acid. $H_3BO_3(H_2B_4O_7)$.	White pr. difficultly sol. in water, sol. in acids.	White pr. sol. in acids.	White pr. sol. in HNO_3, in NH_4OH.
Phosphorous Acid. H_3PO_3.	White pr. sol. in $HC_2H_3O_2$.	White pr. sol. in NH_4Cl.	White pr. but deposits black Ag on warming.
Silicic Acid. H_2SiO_3.	White pr.	White pr.	Yellow pr. sol. in conc. solutions, sol. in HNO_3.
Carbonic Acid. H_2CO_3.	White pr. sol. in acids.	White pr.	White pr. sol. in HNO_3.

THE ACID IONS.

Acids.

Lead Acetate.	Characteristic Reactions.
Wh. pr. sol. in NaOH, in ammonium tartrate, in am. acetate.	Sulfates when heated with Na_2CO_3, in the reducing flame on charcoal give a hepar (Na_2S) which blackens silver, when moistened with water.
———	The potassium and sodium salts are difficultly soluble. Fluosilicates give with conc. H_2SO_4, H_2F_2 and SiF_4.
White pr.	Sulfites reduce $KMnO_4$, give a hepar with Na_2CO_3 on charcoal. Give SO_2 without separation of S, on warming with HCl.
White pr. on boiling becomes gray, $PbS + PbSO_4$.	Gives on warming with HCl, SO_2 and a pr. of S. Gives a hepar with Na_2CO_3 on charcoal. $Na_2S_2O_3$ dissolves AgCl.
White pr. sol. in NaOH, insol. in NH_4OH.	Added to a solution of ammonium molybdate in HNO_3, gives a yellow pr. of ammonium phosphomolybdate; $MgCl_2 + NH_4OH + NH_4Cl$ precipitate white cryst. $MgNH_4PO_4$.
White pr. sol. in an excess of the pyrophosphate.	Does not coagulate albumen. Changed to H_3PO_4 by boiling with HNO_3.
White pr.	Coagulates albumen. Changed to H_3PO_4 by boiling with HNO_3.
White pr. sol. in HNO_3 insol. in $HC_2H_3O_2$.	Yellow precip. with $(NH_4)_2MoO_4$. White precip. with $NH_4Cl + NH_4OH + MgCl_2$.
White pr. sol. in HNO_3 soluble in $HC_2H_3O_2$.	Marsh's test gives an arsenic mirror. H_2S precipitates yellow As_2S_3 from the warm acid solution.
Yellow pr. sol. in NaOH.	Reduced to green $CrCl_3$ by warming with HCl and alcohol.
White pr. sol. in excess of the lead salt.	With alcohol and conc. H_2SO_4 colors flame green. Turmeric paper dipped in the HCl solution becomes red on drying; turns green with NaOH.
White pr. insol. in $HC_2H_3O_2$.	Reducing agent. Very concentrated solutions evolve PH_3 on heating.
White pr. insol. in HNO_3.	Evolves CO_2 with Na_2CO_3 bead. Gives a skeleton of SiO_2 with $NaPO_3$ bead. SiO_2 separates on evaporating the acid solution to dryness.
White pr. sol. in HNO_3.	Effervesces with HCl giving CO_2 which renders lime water turbid.

I.—Inorganic

Salts of	Barium Chloride.	Calcium Chloride.	Silver Nitrate.
Hydrofluoric Acid. H_2F_2.	White pr. sol. in hot HCl.	White, gelatinous pr., sol. in HCl, insol. in $HC_2H_3O_2$.	——
Iodic Acid. HIO_3.	White pr. sol. in HCl.	——	White pr., sol. in NH_4OH. Reduced to AgI by SO_2.
Hydrochloric Acid. HCl.	——	——	White pr., insol. in HNO_3, soluble in NH_4OH, in KCN.
Hydrobromic Acid. HBr.	——	——	Yellowish-white pr., difficultly sol. in NH_4OH. Insol. in HNO_3.
Hydriodic Acid. HI.	——	——	Yellow precip. insol. in NH_4OH, in HNO_3.
Hydrocyanic Acid. HCN.	——	——	White precip. sol. in NH_4OH, in KCN.
Hydroferrocyanic Acid. $H_4Fe(CN)_6$.	——	——	White pr. soluble in KCN, insoluble in HNO_3.
Hydroferricyanic Acid. $H_3Fe(CN)_6$.	——	——	Orange pr. sol. in NH_4OH, in KCN, insol. in HNO_3.
Thiocyanic Acid. HSCN.	——	——	White precipitate, difficultly sol. in NH_4OH.
Nitrous Acid. HNO_2.	——	——	White pr. sol. in hot water.
Hypochlorous Acid. HClO.	——	——	White pr. of AgCl.
Hydrosulfuric Acid. H_2S.	——	——	Black precipitate, soluble in hot HNO_3.
Nitric Acid. HNO_3.	——	——	——
Chloric Acid. $HClO_3$.	——	——	——

Acids.

Lead Acetate.	Characteristic Reactions.
White precipitate, sol. in HNO_3.	With conc. H_2SO_4 gives H_2F_2, which etches glass.
White precipitate.	With KI and $HC_2H_3O_2$, gives free I_2.
White precipitate, soluble in hot water.	With H_2SO_4 and MnO_2 gives Cl_2. With conc. H_2SO_4 and $K_2Cr_2O_7$ gives CrO_2Cl_2.
White precipitate, slightly soluble in hot water.	Cl_2 water liberates Br_2 which dissolves in CS_2 to a reddish-yellow solution.
Yellow precipitate, slightly soluble in hot water.	Cl_2 water, or nitrous acid, liberates I_2, which dissolves in CS_2 to a violet red solution, or colors starch paste blue.
White precipitate, soluble in HNO_3.	After warming with $FeSO_4$, $FeCl_3$ and NaOH, on adding HCl, Prussian blue remains undissolved. When warmed with yellow $(NH_4)_2S$, NH_4SCN is formed.
White precipitate.	Gives Prussian blue with ferric salts. Gives a red precipitate with Cu salts.
No pr. in alkaline solutions, but on warming PbO_2 is precipitated.	Gives a dark blue precipitate with ferrous salts.
White precipitate.	Blood-red color with $FeCl_3$, not destroyed by boiling, but which vanishes on adding $HgCl_2$.
———	Gives a yellow color with meta-phenylene-diamine in acid solution.
White pr. changing to orange, red and br'n on boiling.	Gives with $MnSO_4$ a brownish-black pr. of MnO_2.
Black precip. sol. in hot HNO_3.	Sulfides give a hepar with Na_2CO_3. See sulfates. Soluble sulfides give a violet color with sodium nitroprussiate.
———	Mixed with $FeSO_4$ and poured on conc. H_2SO_4, gives a dark brown zone. Colors a solution of brucine in H_2SO_4, red.
———	Chlorates deflagrate on charcoal. Added to conc. H_2SO_4 they give yellow ClO_2.

II.—Organic

Salts of	Calcium Chloride.	Silver Nitrate.
Formic Acid. $HCHO_2$.	———	White precipitate in conc. solutions, becoming dark from reduction to Ag.
Acetic Acid. $HC_2H_3O_2$.	———	White precipitate, soluble in hot water.
Oxalic Acid. $H_2C_2O_4$.	White precipitate, insoluble in $HC_2H_3O_2$.	White precipitate, soluble in HNO_3.
Tartaric Acid. $H_2C_4H_4O_6$.	White precipitate, soluble in NaOH, reprecipitated by boiling but dissolves again on cooling.	White precipitate with alkali salts, soluble in HNO_3 and in NH_4OH. Precipitate or mirror of Ag on warming.
Malic Acid. $H_2C_4H_4O_5$.	White precipitate only in presence of strong alcohol.	White precipitate.
Citric Acid. $H_3C_6H_5O_7$.	White precipitate, less soluble in hot than in cold water. Insoluble in NaOH, soluble in NH_4Cl.	White precipitate.

Salts of	Ferric Chloride.	Silver Nitrate.
Benzoic Acid. $HC_7H_5O_2$.	Flesh colored precipitate, soluble in HCl.	White precipitate, soluble in hot water.
Succinic Acid. $H_2C_4H_4O_4$.	Pale red precipitate.	White precipitate.
Salicylic Acid. $HC_7H_5O_3$.	Deep violet color.	White precipitate, soluble in hot water.
Gallic Acid. $C_7H_6O_5$.	Blue black precipitate.	Reduces to metallic Ag.
Tannic Acid. (Tannin.) $C_{14}H_{10}O_9$.	Blue black color.	White precipitate.

Acids.

Lead Acetate.	Characteristic Reactions.
———	Reducing agent, with conc. H_2SO_4 gives CO.
———	Gives with $FeCl_3$ a reddish-brown solution and a precipitate on boiling. Alcohol and conc. H_2SO_4 give ethyl acetate, $(C_2H_5)C_2H_3O_2$, recognized by its odor.
White pr. sol. in HNO_3 and in NH_4OH.	Heated with conc. H_2SO_4 gives CO_2 and CO. With dil. H_2SO_4 and MnO_2 gives CO_2.
White pr. sol. in NaOH.	The acid K and NH_4 salts are difficultly soluble.
White pr. which melts under boiling water.	
White pr. sol. in ammonium citrate.	Tartaric, malic and citric acids prevent the precipitation of $FeCl_3$ by alkalies.

Lead Acetate.	Characteristic Reactions.
White pr.	Melts at 121°.
White pr.	Melts at 180°.
White pr.	Melts at 156°.
———	Melts at 200°. The alkaline sol. absorbs O_2.
Yellow pr.	Amorphous, with an astringent taste. It precipitates a solution of glue.

PART II.

SYSTEMATIC ANALYSIS.

Before beginning the analysis of an unknown substance, the analyst should consider the amount at his disposal. Portions will be needed for preliminary examination, for the detection of metals, and for the detection of acids; *such quantities should be used in these operations that at least one-third may remain for cases of emergency.*

The quantity of substance taken for analysis should always be approximately known, for a good qualitative analysis should show, besides the presence or absence of various elements, also their approximate relative quantities. Commercial calcium bisulfite solution, for example, which is largely used in the manufacture of paper, almost always contains as impurities relatively small amounts of sodium, magnesium, iron, sulfate, chloride, etc. If an analyst, after having found all these substances, should report simply that the substance was a solution in water of the chlorides, sulfites, and sulfates of sodium, magnesium, calcium, iron, etc., his report would be very misleading. The report should be, that the substance is approximately a 10 per cent. solution of calcium bisulfite in water, containing very small quantities of sodium, magnesium, chloride, sulfate, etc., as impurities.

A. DETECTION OF THE METALLIC IONS.

PREPARATION OF THE SOLUTION.

Preliminary Examination.—If the substance is a solid, note its color, odor, and texture; determine, if possible, whether it is a mixture and, if so, note the appearance of its components.[1] Especially note whether it is an alloy, and, if it is not an alloy, determine whether it contains organic matter or water by heating about 0.1 gram of the finely powdered substance in a hard glass tube closed at one end; heat gently at first, keeping the upper part of the tube cool so that any water present may condense there, and then heat strongly. Note whether the substance blackens, whether a tarry or aqueous deposit forms on the cold part of the tube, and whether a burnt odor is emitted.

If the substance is a solution containing a volatile solvent, note its odor, test it with litmus paper, and evaporate a small sample to dryness on a watch glass over a beaker of boiling water to ascertain if it contains any non-volatile material at all. If a dry residue remains, estimate the amount of solution that should be used to contain about 1 gram of the solid material. Test the residue for organic matter as described in the preceding paragraph.

A. Organic Matter is Absent.

I. The Substance is a Solution.—If neutral or acid, proceed with the usual analysis for cations and anions, beginning with (1), Part I. Strongly alkaline solutions may contain such substances as silicates of the alkali metals, thioarsenates, thioantimonates, thiostannates, ammonia complexes, complex cyanides, etc., which upon acidification give precipitates. In such a case, proceed directly to II (b) below.

II. The Substance is a Solid, but not a Metal or Alloy.—Grind to a very fine powder in a clean mortar, measure out about 1 gram, and treat it with the following solvents in the order named:

(a) *Water.*—Add 10 to 20 cc. of water, heat to boiling, and test the solution with litmus paper. If the substance dissolves completely to a neutral or acid solution, proceed according to the usual method for the detection of cations and anions. (See Part I, pp. 18, 60.) But if there is a residue, or if the solution is strongly alkaline, proceed directly, without filtering, to (b) below.

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[1] A lens or a microscope, if necessary, should be used at this point.

(b) *Nitric Acid.*[1]—To the solid substance (or the solution from (a) above) add 5 to 10 cc. of conc. HNO_3, and evaporate just to dryness. Now gently heat over a small flame, kept in constant motion, for a minute or so. (Or better, heat in a drying oven at 120–130° for at least half an hour.)[2] Rub the residue to a fine powder with a blunt rod; add to it 5 to 10 cc. of dil. HNO_3, cover the beaker and heat on the steam bath for 10 minutes. Dilute with 20 cc. of water, heat to boiling, filter, and wash the residue. Treat the residue by (c) below. Save the solution to be combined with the solution or solutions obtained later from the residue.

(c) *Concentrated HCl.*—To the residue from (b) above add gradually 5 to 10 cc. of conc. HCl, and heat under a hood as long as action continues, adding more HCl if necessary. If the substance dissolves completely, combine it with the solution obtained in II (b) above; if the substance does not dissolve completely proceed without filtering to (d).

(d) *Aqua Regia.*—To the mixture from (c) add one-third its volume of conc. HNO_3, and heat as long as action continues, adding more of the acids if necessary. Combine the solution with the one obtained in (b). Save the residue for (e).

The solutions obtained in (b), (c) and (d) should be combined and analyzed for the metallic ions. Since the solutions from (c) and (d) contain HCl, Group I of the cations will be present as a precipitate. Filter, wash, and test the precipitate for the members of Group I according to (2), (3) and (4), Part I, page 19. Test the filtrate for the members of the remaining groups.

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[1] *In dissolving solid substances* either HNO_3 or HCl may be first used, each having advantages and disadvantages of its own. Owing to its oxidizing properties, HNO_3 dissolves many alloys and sulfides not attacked by HCl, but it fails to dissolve certain oxides (such as MnO_2, Sb_2O_5, and hydrated SnO_2) which dissolve in HCl. HCl may cause the precipitation of Group I; while strong HNO_3 on heating oxidizes sulfides partially to sulfates and may cause the precipitation of Pb, Ba, Sr, and Ca as sulfates. HNO_3 oxidizes mercurous, arsenious, antimonious, stannous, and ferrous compounds to the higher state of oxidation. If HCl alone were used as a solvent, Hg, and As, if present in the arsenious condition, would be partly or wholly lost (owing to the volatility of their chlorides) in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and also because the procedure is a more general one, the use of HNO_3 is recommended. *If, however, organic matter and silica are absent and the substance dissolves completely in HCl, considerable time may be saved by using HCl and omitting the evaporation.* An excess of HCl must be avoided, however. Furthermore, certain amounts of As and Sb would be lost as AsH_3 and SbH_3 if the substance is an alloy.

[2] In the case of non-metallic substances which do not contain silica, the evaporation and subsequent heating at 120–130°, etc. (see IV.), may be omitted. In that case, heat on a steam bath for 10 minutes, and proceed as described in the last of the paragraph. With respect to the use of HCl instead of HNO_3, see footnote above.

(e) *Ammonium Hydroxide.*—Extract the residue several times with a 5 cc. portion of NH_4OH. Filter and acidify the filtrate with dil. HNO_3. A white precipitate is AgCl. If AgCl is found continue the washing with NH_4OH until the AgCl is completely removed. Reserve the residue for (f).

Note.—The aqua regia treatment in (d) converts all the insoluble Ag compounds remaining in the residue (*i. e.*, AgCl, AgBr, AgI and AgCN) into AgCl.

(f) *Sodium Carbonate Solution.*—Transfer the residue from (e) to a Pyrex beaker, add about 25 cc. of conc. Na_2CO_3 solution, cover with a watch glass, and boil for 10 minutes. Filter, and wash the residue thoroughly. The filtrate should be tested for the SO_4^{--} anion, which would indicate that the residue contained such substances as $PbSO_4$, $CaSO_4$, $SrSO_4$ and possibly $BaSO_4$. Heat the residue from the Na_2CO_3 extraction with 5 cc. of dil. HCl, and add 10 cc. of water; filter, wash the residue, and save it for (g). Dilute the filtrate to 40 cc., treat the solution with H_2S, and test only for Pb, Bi, Sb, Cr, Ba, Sr and Ca.

(g) *Fusion with Na_2CO_3.*—Transfer the residue from (f) to a platinum crucible,[1] ignite until the filter is destroyed, mix the residue with 5 to 10 grams of anhydrous Na_2CO_3 and 0.1 to 0.5 gram solid KNO_3, cover the crucible, and heat for 10 minutes over a blast lamp, or until the melt ceases to effervesce or show any sign of action, adding more Na_2CO_3 if necessary. Cool, place the crucible in a beaker, carefully add dil. HCl till the solution is strongly acid, evaporate to dryness, and heat to 120–130° to render silica insoluble; add 4 cc. of dil. HCl and 10 to 20 cc. of water, boil and filter. Dilute the filtrate to 40 cc. and treat by Part I, beginning with (5), p. 23, testing for all the cations except those of the alkali metals. Test the residue for SiO_2 by the metaphosphate bead test (page 74).

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[1] No substance containing Ag, Pb, Bi, As, Sb or Sn should be heated in a platinum crucible.

(h) *Special Methods.*—There are certain substances which require special treatment to bring about their solution:

Native SnO_2 (cassiterite or tinstone) is heated in a porcelain crucible with six times its weight of a mixture of anhydrous Na_2CO_3 and S (equal parts). The crucible is covered with a lid, and heated over a small flame until the excess of sulfur has distilled off and burned. The operation requires about 20 minutes. Allow the crucible to cool and then treat its contents with hot water, filtering out any of the undissolved residue, which may contain FeS and other sulfides.

Calcium Fluoride, CaF_2 (fluorite or fluospar), and Na_3AlF_6 (cryolite) are decomposed by heating with conc. H_2SO_4, or by fusing with $NaHSO_4$, in a platinum crucible or dish. Glass would be attacked by the H_2F_2 evolved. In the case of CaF_2, the Ca remains mainly in the residue as $CaSO_4$.

Insoluble Complex Cyanides (Prussian blue, $Fe_4(Fe(CN)_6)_3$, and Turnbull's blue, $Fe_3(Fe(CN)_6)_2$ are completely decomposed by boiling with NaOH solution. The Fe is precipitated as $Fe(OH)_3$ and $Fe(OH)_2$ and the CN radical goes into solution as NaCN.

Ignited Al_2O_3 (corundum) and *Cr_2O_3* (chrome green) are best brought into solution by fusing with 10 parts of $NaHSO_4$ in a platinum crucible or dish.

III. The Substance is a Metal or Alloy. Weigh out into a Pyrex beaker or dish about 0.5 gram of the metallic substance, which should consist of as small particles as possible so as to facilitate its action with solvents. The proper solvent is best chosen by actual trial. It is suggested that the following solvents be tried in the order given:

(a) *Dilute HNO_3.*—Add to the substance in the beaker about 10 cc. of dil. HNO_3, cover with a watch glass, and heat on a steam bath as long as any action continues, adding a little conc. HNO_3 from time to time if the action is renewed thereby, or a little water if crystalline salts are deposited. If the substance dissolves completely, proceed directly to the last paragraph in this section; if the HNO_3 appears to have little action,[1] or if a white precipitate separates, proceed at once to (b).

(b) *Aqua Regia.*—Add at once to the HNO_3 in contact with the metallic substance 5 cc. of conc. HCl, and heat on a steam bath until the reaction is complete.[2]

Evaporate the solution from (a) or (b) just to dryness. Rub the mixture to a fine powder with a blunt glass rod, add 4 cc. of dil. HCl and about 10 cc. of water. Cover with a watch glass, and heat just to boiling, being careful not to lose any of the acid by boiling. Filter and wash thoroughly. The residue contains Group I as chlorides, and the filtrate the subsequent groups. Proceed with the cation analysis [3] as directed in Part I, p. 19.

B. Organic Matter is Present.

Certain kinds of organic matter, especially hydroxy compounds such as the sugars, tartaric acid, etc., prevent the precipitation of aluminium and chromium hydroxides, and must therefore be removed.[4] Moreover, a large quantity of organic matter of any kind interferes with the operations of solution, filtration and evaporation.

Powder, or cut into small pieces 1 to 5 grams of the substance (according to the amount of organic matter present). Add to it in a Pyrex beaker about 5 cc. conc. H_2SO_4; warm gently until well charred; cool; add slowly, with constant stirring, under a hood, conc. HNO_3 until violent action ceases; digest for some time on a steam bath, and then heat over a flame, stirring constantly, until the substance is thoroughly charred. Cool, again add conc. HNO_3 as before, and heat until dense white fumes of H_2SO_4 are evolved; cool, and add a little conc. HNO_3. Repeat this process till the H_2SO_4 becomes light colored and remains so when strongly heated. Evaporate the remaining H_2SO_4 under a hood to about 1.5 cc. Cool thoroughly and add the contents of the beaker to about 10 cc. of water in another beaker; then pour the liquid back into the first beaker, rinsing out the second beaker with a little water. If there is a residue, cover the beaker and boil for some time (to extract slowly dissolving sulfates, such as anhydrous $Fe_2(SO_4)_3$). Cool, filter, and wash, first with dil. H_2SO_4 and then with a little water, rejecting the washings. Treat the residue[1] by II (f). To the solution add a drop of dil. HCl. If a precipitate forms, add dil. HCl drop by drop *only as long as the precipitate continues to form;* filter, wash the precipitate, and test it for silver. Dilute the solution to a volume of 40 cc., and treat it by (**5.**), Part I, p. 23.

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[1] Certain metals are not brought into solution by HNO_3: Gold and platinum are not attacked at all; tin is converted into the insoluble metastannic acid, $(H_2SnO_3)_x$; antimony into $Sb_2O_{3\text{-}5}$; and a number of other metals, as Al, Fe and Cr, become "passive"; Ni and Co show the phenomenon of passivity to a lesser degree. In case, then, there is little action with HNO_3, or a white precipitate forms, a different solvent is indicated.

[2] A black residue insoluble in aqua regia may contain carbon or carbides, or certain alloys of iron, as ferrochrome or ferrosilicon.

[3] The alkali and alkaline earth metals are never found in the commoner alloys; that is, Mg is the only metal of Groups IV and V that need be tested for in alloys which do not decompose water.

[4] In the case of substances like oil paints, it is often best to simply extract the oil with ether, and then to treat the residue by (II, page. 95)

B. DETECTION OF THE ACIDIC IONS.

Preliminary Examination.—Moisten a small quantity of the finely powdered solid in a small test-tube with water, and then add about 1 cc. conc. H_2SO_4; in this way considerable heat is evolved, and it is usually unnecessary to warm the tube. The indications which may be derived from this test have already been discussed in Part I, p. 64, which see.

General Procedure.—The procedure to be followed is that given under Anion Analysis in Part I. Frequently this may be modified and shortened, if the general nature of the unknown substance is known, thereby limiting the anions that might be present to a relatively small number.

[1] This residue may contain silicates; all the Pb, Ba, and Sr that were present in any form; all the silica; some of the Ca, Bi, Sb, and Sn; and practically all of the Cr.

a. Salts and Industrial Products.

If the substance is soluble in water, and only alkali and alkali earth metals are present, dissolve about 1 gram of it in 20 to 30 cc. water, and use this solution for the $AgNO_3$ and $Ba(NO_3)_2$ tests,[1] and for the various special tests described in Part I; if, however, other metals are present, add to the boiling-hot solution of the substance in water Na_2CO_3 solution as long as a precipitate continues to form. Filter off, and reject the precipitate; use the filtrate for the $AgNO_3$ and $Ba(NO_3)_2$ tests and for the various special tests, as described below.

If the substance is insoluble, and metals not precipitated by H_2S are present, boil 1 gram of the finely powdered substance in a porcelain dish with about 10 cc. conc. Na_2CO_3 solution for at least 10 minutes, replacing the water which evaporates. Filter, and neutralize half of the filtrate with HNO_3; filter off any precipitate, slightly acidify the filtrate with HNO_3, boil to expel the CO_2, and use the solution for the $AgNO_3$ and $Ba(NO_3)_2$ tests, and for the special tests which may be made in the presence of HNO_3. Acidify fresh portions of the Na_2CO_3 solution with $HC_2H_3O_2$ for the oxalic and tartaric acid tests, and with H_2SO_4 for the nitric acid test. If, however, only metals which are precipitated by H_2S are present, and if chlorates and nitrates [2] are known to be absent, suspend a gram of the finely powdered substance in 50 cc. of water, saturate with H_2S, heat to boiling, and filter; boil the filtrate till the H_2S is entirely expelled, and use it for the $AgNO_3$ and $Ba(NO_3)_2$ tests, and for the various special tests.

If not already detected or proved absent, test the original substance for H_2S, H_2CO_3, H_2SO_3 and $H_2S_2O_3$.

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[1] H_3BO_3 is precipitated by $Ba(NO_3)_2$ only from fairly concentrated solutions; it should also be noted that BaF_2 as well as many of the barium salts of Group III are fairly soluble in ammonium salt solutions. For that reason, ammonium salts, if present, should first be removed by boiling with carbonate-free NaOH solution.

[2] In the presence of such oxidizing substances it is better to prepare the solution by the Na_2CO_3 method; otherwise, in the presence of chlorates, the tests for HCl and H_2SO_4 would be valueless, and in that of nitrates the H_2SO_4 test would be uncertain.

All the metals except arsenic and the alkalies are precipitated from solution by Na_2CO_3 as carbonates, basic carbonates, or hydroxides. Moreover, most insoluble salts are more or less completely decomposed by a boiling-hot, concentrated solution of Na_2CO_3, the acid radical going into solution; many of the carbonates and hydroxides are somewhat soluble in the excess of Na_2CO_3, but they are re-precipitated when the solution is neutralized. The solution must be slightly acidified, and the CO_2 expelled before testing with $AgNO_3$ and $Ba(NO_3)_2$; otherwise Ag_2CO_3 and $BaCO_3$ will precipitate.

The removal of the metals with H_2S, while more complete than with Na_2CO_3, is of course inapplicable in the presence of strong oxidizing agents, such as chlorates, etc.

b. Minerals and Metallurgical Products.

First try the special tests for H_2S and H_2CO_3 with portions of the finely powdered substance, unless these have already been detected.

Boil about 1 gram of the powdered substance with 5 cc. conc. HNO_3 for 2 or 3 minutes, add 15 cc. water, boil again, and filter from any residue. Test portions of the filtrate for H_3PO_4 with ammonium molybdate reagent, and for HCl with $AgNO_3$ solution. If sulfides are absent, test a portion for H_2SO_4 with $Ba(NO_3)_2$ solution; if the substance was not completely dissolved by the HNO_3, fuse the residue with 3 or 4 parts solid Na_2CO_3, boil the fused mass with water, filter, and test the filtrate for H_2SO_4 by acidifying it with HCl and adding $Ba(NO_3)_2$ solution.[1] If sulfides are present, boil some of the finely powdered original substance with conc. Na_2CO_3 solution for 5 or 10 minutes, filter, acidify the filtrate with HCl, and add $Ba(NO_3)_2$.[2]

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[1] If Ag has been found among the metals, the solution obtained by boiling or fusing with Na_2CO_3 must also be tested for HCl, etc.

[2] Sulfides are partially oxidized to sulfates by boiling with HNO_3 and by fusing with Na_2CO_3; hence the substance should be boiled with Na_2CO_3 solution, or, if completely soluble in acid, it may be dissolved in HCl and the solution tested for H_2SO_4 in the presence of H_2S.

The presence or absence of silicic acid will always have been determined in the analysis for metals. If silicates are absent, test for H_2F_2 with H_2SO_4, and for H_3BO_3 with H_2SO_4 and alcohol. If silicates are present, it is necessary in testing for these acids to fuse about 1 gram of the powdered substance with 4 or 5 parts of Na_2CO_3.[1] Boil the fused mass with 15 to 20 cc. of water and filter; slightly acidify a portion of the filtrate with HCl and test it for H_3BO_3 with turmeric paper; evaporate half of the remaining filtrate to dryness and test for H_3BO_3 with H_2SO_4 and alcohol. Acidify the remainder of the filtrate with $HC_2H_3O_2$, allow the mixture to stand, filter off the precipitate of silicic acid, and add $CaCl_2$ solution; allow the mixture to stand, filter, and test the precipitate for H_2F_2 with H_2SO_4.

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[1] All silicates are not decomposed by H_2SO_4, and even if they were, H_2F_2 might be completely changed to SiF_4 by the SiO_2 present.

SPECIAL PART.

In many cases the method of procedure in qualitative analysis can be shortened because the chemist knows beforehand what substances are likely to be present. In other cases special methods are necessary for the purpose of detecting minute amounts of elements or compounds. In the directions given below it is presupposed that a knowledge of the methods of analysis has already been acquired, and that the student will know how to interpret his results.

POTABLE WATERS.

By noticing carefully the amounts of the precipitates and the intensity of the reactions obtained, a qualitative analysis may give considerable information with regard to the character of a given water.

Evaporate 250 cc. of the water in a porcelain dish to one-third, filter, and save both precipitate and filtrate.

EXAMINATION OF THE PRECIPITATE.

Dissolve in the least possible amount of dil. HCl, noting the presence or absence of carbonates. Test separate portions of the solution:

1. For Fe^{+++} with NH_4SCN.
2. For Ca^{++} with NH_4OH and $(NH_4)_2C_2O_4$. Warm, filter and test the filtrate for Mg^{++} with Na_2HPO_4.
3. For SO_4^{--} with $BaCl_2$. If found, $CaSO_4$ is indicated.
4. For PO_4^{---}. Add HNO_3, evaporate to dryness, moisten with HNO_3, filter from any silica which remains, add to the filtrate an equal volume of molybdic solution and allow to stand over night.

EXAMINATION OF THE FILTRATE.

Test separate portions:

1. For SO_4^{--} with dil. HCl and $BaCl_2$.

2. For Cl^- with dil. HNO_3 and $AgNO_3$.

3. A larger portion for PO_4^{---} by evaporating with HNO_3 as above in 4.

4. About 10 cc. for NO_3^- by evaporating to a few drops and adding carefully to 2 cc. of conc. H_2SO_4 in which a minute amount of brucine has been dissolved. The solution must be almost or quite colorless before the water is added, otherwise the H_2SO_4 contains nitric acid and is unfit for the test.

5. Add to the remainder of the solution NH_4Cl, NH_4OH and $(NH_4)_2C_2O_4$ to test for Ca^{++}. If much Ca is found here, it must have been present as a sulfate, chloride or nitrate. Warm for some time, filter and test a *small portion* of the filtrate with Na_2HPO_4 and NH_4OH for Mg^{++}. Evaporate the remainder of the solution to a few drops and test with the spectroscope for K and Na. Lithium may sometimes be found here. The ordinary tests for K and Na may also be used after removing the Mg.

FURTHER TESTS.

Carbonic Acid.—Put 3 cc. of lime water in a test-tube and add a little of the water. A precipitate which redissolves on adding more of the water indicates free H_2CO_3.

Nitrous Acid.—To about 50 cc. of the water to be tested add 2 cc. of the α-naphthylamine-sulfanilic acid reagent (see *Nitrite*, p. 69), stir, and allow the mixture to stand for 5 or 10 minutes.

Ammonia and Nitrogenous Organic Matter.—Take a *clean* 300 cc. distilling bulb, closed with a *cork*, put in it 100 cc. of distilled water and 2 cc. of a solution of Na_2CO_3. Distil through a Liebig's condenser till 10 cc. of the distillate gives no reaction for ammonia with Nessler's solution. Add 100 or 150 cc. of the water, distil 10 cc. and test the distillate with Nessler's solution. If ammonia is found, distil till the distillate is free from ammonia, then add 10 cc. of an alkaline solution of potassium permanganate [1] which has been diluted with 20 cc. of water and boiled down to its original volume in a 100 cc. flask. Distil 10 cc. and test the distillate with Nessler's solution. The potassium permanganate oxidizes the organic matter in the water and at the same time a part of the nitrogen of the organic matter is converted into ammonia. Such ammonia is commonly called "albuminoid ammonia."

These tests require the most extreme care in every detail, and are entirely worthless if any one works with solutions containing ammonia in the neighborhood of the apparatus.

Organic Matter.—Put 200 cc. of the water in a clean flask, add 10 cc. dil. H_2SO_4 and then a dilute solution of $KMnO_4$[2] drop by drop till the water acquires a faint pink color which does not disappear on standing 2 or 3 minutes. Then add 1 cc. $KMnO_4$ and heat to boiling. If the pink color disappears, add more of the solution, noting the amount. The $KMnO_4$ is reduced by the organic matter in the water.

Hydrogen Sulfide.—Fill a bottle two-thirds full with the water, suspend a strip of paper moistened with a solution of lead acetate from the stopper, and allow to stand for about 1 hour. If the paper turns dark, H_2S is indicated. If the paper does not blacken, add to the water dil. HCl and repeat the test. Blackening now indicates a *sulfide.*

Lead.—Add 5 cc. of NH_4OH to 2 or 3 liters of the water, then acetic acid to acid reaction, evaporate to about 10 cc., filter and test the filtrate with H_2S. If a black precipitate forms, test this for lead.

Aluminium.—Take 500 cc. of the water, add 100 cc. of lime water, heat rapidly till a copious precipitate forms and filter as quickly as possible, best with a filter plate and pump. Dissolve the precipitate in dil. HCl, evaporate to dryness in a platinum dish and dry at 120–130° to separate silica, moisten the residue with conc. HCl, dilute slightly, filter and test the filtrate for Fe and Al by adding NH_4OH. It is usually possible to tell whether Al is present or not by the appearance of the precipitate. If the result is doubtful, filter, dissolve in HCl, add a little pure NaOH and boil in a platinum dish, filter and test the filtrate for Al by adding HCl and NH_4OH. This method will enable the chemist to distinguish between soluble aluminium compounds and clayey matters, only the former being shown by this treatment.

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[1] Eight grams $KMnO_4$ and 200 grams KOH to one liter of water.

[2] 0.395 gram $KMnO_4$ to 1 liter. One cc. contains 0.1 milligram available oxygen.

IRON AND STEEL.

The following tests may be of considerable value in the comparison of specimens of iron and steel if the amounts taken are weighed roughly and the methods of testing the two specimens are exactly alike.

Phosphorus.—Take 0.2 gram, dissolve in 5 cc. HNO_3,[1] filter, add a little $KMnO_4$ and boil, then a drop of ammonium tartrate or of tartaric acid, boil till clear, add NH_4OH till nearly neutral but still perfectly clear and distinctly acid, and then add 5 cc. of molybdic solution.

Sulfur.—Dissolve from 1 to 5 grams in dil. HCl and pass the gas evolved through a solution of caustic soda to which a little lead acetate has been added.

Silicon.—Dissolve 0.2 gram. in 5 cc. HNO_3, add 8 cc. dil. H_2SO_4 and evaporate till fumes of H_2SO_4 appear. Cool, add water and dil. HCl; warm, filter, wash thoroughly and ignite the residue in a porcelain crucible over the blast till only white SiO_2 remains. Test this with the metaphosphate bead (see page 74).

Graphite.—This will be found in the residue left when iron is dissolved in dil. HCl.

Combined Carbon.—Dissolve 0.4 gram in 4 cc. of HNO_3 by heating in a test-tube immersed in boiling water. The depth of color indicates the amount of combined carbon present and may be used for the comparison of specimens of steel of the same character. Both graphite and combined carbon are left undissolved when iron or steel is dissolved in a solution of the double chloride of copper and ammonium.

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[1] In all tests given here, sp. gr. = 1.20.

Manganese.—Dissolve 0.1 gram in 10 cc. HNO_3, filter, evaporate to a volume of 2 or 3 cc., add about 0.5 gram solid $KClO_3$, and boil gently. If a brown substance separates, filter it off, using an asbestos filter, and warm it with 5 or 10 cc. HNO_3 and about 0.5 gram PbO_2. Pour the mixture into a test-tube, allow the excess of PbO_2 to settle, and note the color of the solution.

SILVER AND GOLD ORES.

If the amount of silver is considerable, the tests given in the regular course of analysis may be applied. The silver is frequently present as a chloride, however, and must be dissolved in a solution of KCN, precipitated with H_2S or $(NH_4)_2S$, and the Ag_2S dissolved by boiling with HNO_3.

When the amount of silver or gold is small, the most satisfactory method is to fuse 25 to 100 grams of the powdered ore with $NaHCO_3$, PbO and argol (crude cream of tartar). The lead button obtained is then scorified and cupelled. The following charge answers well with most siliceous ores: Ore, 60 grams; $NaHCO_3$, 60 grams; PbO, 50 grams; argol, 4 grams. If the ore is basic, add 40 grams of silica and use a little less soda. Ores containing sulfides must be roasted. The fusion may be made in a Hessian crucible in a gas furnace, or in an ordinary coal fire. For fuller details, a book on assaying should be consulted.

APPENDIX.

Form of Record.

It is essential that in performing the preliminary experiments such a record shall be kept of the work that afterward it will be possible, by referring to it, to determine where each metal goes at every stage of the analysis. *This thought should be kept constantly in mind in making the record.* It is not necessary, however, to repeat statements from the text-book, and the more concise the record can be made the better, provided it contains all essential facts and is clear. An illustration will, perhaps, be of service.

Silver.

$AgNO_3 + HCl = \underset{\text{White ppt.}}{\underline{AgCl}} + HNO_3.$

$AgCl$ + hot water—does not dissolve, since the filtrate gives no ppt. with H_2S.

$AgCl + 2NH_3 = \underset{\text{Clear sol.}}{Ag(NH_3)_2Cl}.$

$Ag(NH_3)_2Cl + 2HNO_3 = \underset{\text{White ppt.}}{\underline{AgCl}} + 2NH_4NO_3.$

In recording analyses, one of the following forms will be found convenient:

No.	Substance.	Reagent.	Result.	Inference.	Precip. or residue.	Solution.
1	Colorless sol.	HCl.	Wh. pr.	Gr. I.	$AgCl$, Hg_2Cl_2, $PbCl_2$.	
2	Pr. 1.	Hot H_2O.	Partial sol.		$AgCl$, Hg_2Cl_2.	$PbCl_2$.
3	Sol. 2.	H_2SO_4.	Wh. pr.	Pb.	$PbSO_4$.	
4	Res. 2.	NH_4OH.	Blackens.	Hg.	$NH_2HgCl + Hg$.	$Ag(NH_3)_2Cl$.
5	Sol. 4.	HNO_3.	No pr.	No Ag.		

The numbers in the second column refer to the operation which gave the precipitate or solution referred to, and any metal can be followed by these numbers from the beginning to the end of the analysis. The columns headed "Precip. or Residue" and "Solution" give the compounds which would be present in each case if all metals of the group were present.

Slightly acid solution: added HCl.

<table>
<tr><td colspan="3">Precipitate: AgCl, Hg_2Cl_2, $PbCl_2$.
Extracted with hot water.</td><td rowspan="5">Filtrate:
Groups I–IV.</td></tr>
<tr><td colspan="2">Residue: AgCl, Hg_2Cl_2.
Treated with NH_4OH.</td><td>Filtrate: $PbCl_2$.
Added $K_2Cr_2O_7$ solution.</td></tr>
<tr><td rowspan="2">Black residue:
NH_2HgCl + Hg.</td><td>Filtrate:
$Ag(NH_3)_2Cl$.
Acidified with HNO_3.</td><td rowspan="2">Yellow precipitate:
$PbCrO_4$.</td></tr>
<tr><td>No precipitate; therefore silver not present.</td></tr>
<tr><td colspan="3">Found present: Lead and mercurous mercury.</td></tr>
</table>

It is important that the record should be made in the laboratory as the experiments are performed.

Be prepared to recite upon the following questions and equations, as far as the point assigned in the lectures.

GROUP I.

Lead.

1. Lead nitrate and hydrochloric acid give?
2. Lead chloride and hot water give?
3. Lead chloride and hydrogen sulfide give?
4. Lead chloride and sulfuric acid give?
5. Lead chloride, potassium dichromate and ? give lead chromate, chromic acid and ?

Mercury in Mercurous Salts.

1. Mercurous nitrate and hydrochloric acid give?
2. Mercurous chloride and hot water give?
3. Mercurous chloride and ammonia give ammonobasic mercuric chloride and ?

4. Ammonobasic mercuric chloride, mercury and *aqua regia* give mercuric chloride, ammonium chloride, nitric oxide, and water. Write first a reaction between ammonobasic mercuric chloride and hydrochloric acid, giving mercuric chloride and ammonium chloride; then a reaction between mercury and *aqua regia*, giving mercuric chloride, nitric oxide and water.

Silver.

1. Silver nitrate and hydrochloric acid give?
2. Silver chloride and hot water give?
3. Silver chloride and ammonia give?
4. Ammonio-silver chloride and nitric acid give?

What ions are furnished by ammonio-silver chloride? Account for the solubility of silver chloride in ammonia, and for its reprecipitation upon acidifying the solution. What equilibria are here involved?

The chlorides of lead, mercurous mercury, and silver are appreciably soluble in concentrated hydrochloric acid. Account for this fact.

Show by means of equations the action of each of the following reagents upon lead, mercurous, and silver salt solutions: Hydrogen sulfide, sodium hydroxide, sodium carbonate.

GROUP II.

A. THE COPPER GROUP.

Mercury in Mercuric Salts.

1. Mercuric chloride and hydrogen sulfide give?
2. Mercuric sulfide and nitric acid give?
3. Mercuric sulfide and aqua regia give mercuric chloride, nitric oxide, sulfur and water.
4. Mercuric chloride and stannous chloride give?
5. Mercuric sulfide and bromine solution give?

What causes the white ppt. formed on the addition of a drop of $SnCl_2$ to $HgCl_2$ solution to turn gray on the addition of more $SnCl_2$?

Lead.

1. Lead chloride and hydrogen sulfide give?

2. Lead sulfide and dilute nitric acid give lead nitrate, nitric oxide, sulfur and water. Write first lead sulfide and nitric acid give lead nitrate and hydrogen sulfide; then hydrogen sulfide and nitric acid give nitric oxide, sulfur and water; then combine the two reactions.

3. Lead nitrate and sulfuric acid give?

Why is it directed in the procedure to evaporate with sulfuric acid at this point to white fumes, and then to dilute the solution again with water?

4. Lead sulfate and ammonium acetate give?

5. Lead acetate, potassium dichromate and ? give?

How does it happen that lead, if present, should always be found in Group II, while it may or may not be detected in Group I?

Bismuth.

1. Bismuth chloride and hydrogen sulfide give?

2. Bismuth sulfide and nitric acid give?

3. Bismuth nitrate and sulfuric acid give? Why is it directed in the procedure at this point to use as much as 3 cc. of concentrated sulfuric acid?

4. Bismuth sulfate and ammonium hydroxide give?

5. Bismuth hydroxide and sodium stannite give metallic bismuth, sodium stannate, and ?

Copper.

1. Copper sulfate and hydrogen sulfide give?

2. Copper sulfide and dilute nitric acid give? (Cf. 2, under Lead.)

3. Copper nitrate and sulfuric acid give?

4. Copper sulfate and ammonia in excess give?

5. Ammonio-cupric sulfate and sulfuric acid give copper sulfate and ?

6. Copper sulfate and iron give?

Cadmium.

1. Cadmium nitrate and hydrogen sulfide give?

2. Cadmium sulfide and dilute nitric acid give? (Cf. 2., under Copper.)

3. Cadmium nitrate and sulfuric acid give?

4. Cadmium sulfate and ammonia in excess give?

5. Ammonio-cadmium sulfate and sulfuric acid give?

6. Cadmium sulfate and iron give?

7. Cadmium sulfate and hydrogen sulfide give?

Account for the solubility of copper and cadmium hydroxides in ammonium hydroxide, giving the equilibria which are involved in the action.

Explain why iron displaces copper ions but not cadmium ions from solution. Could we use zinc instead of iron for the removal of copper, before testing for cadmium? Why?

Explain why copper, while not soluble in hydrochloric acid, will dissolve readily in nitric acid.

Explain the non-precipitation of cadmium by hydrogen sulfide in the presence of much hydrochloric acid. Describe and explain the conditions under which cadmium may be completely precipitated from acid solution by hydrogen sulfide.

Show by means of equations the action of sodium hydroxide, and of sodium carbonate, upon solutions of mercury, lead, bismuth, copper, and cadmium salts.

B. THE TIN GROUP.

Arsenic.

1. Arsenious oxide and hydrochloric acid give arsenic trichloride and ?

2. Arsenic trichloride and hydrogen sulfide give?

3. Arsenious sulfide and ammonium polysulfide give?

4. Ammonium thioarsenate and hydrochloric acid give?

5. Arsenic acid and hydrogen sulfide (in the presence of dilute hydrochloric acid) give arsenic pentasulfide and ?

6. Arsenic acid and hydrogen sulfide (in the presence of ammonium iodide) give arsenic trisulfide and ?

7. Arsenic pentasulfide, ammonium hydroxide and hydrogen peroxide give ammonium arsenate, ammonium sulfate and ?

8. Ammonium arsenate and magnesium chloride (in the presence of ammonium chloride) give?

Antimony.

1. Antimony trichloride and hydrogen sulfide give?
2. Antimony trisulfide and ammonium polysulfide give?
3. Ammonium thioantimonate and hydrochloric acid give?
4. Antimony pentasulfide and concentrated hydrochloric acid give antimony trichloride, sulfur and ?
5. Antimony trichloride and aluminium give?
6. Antimony, hydrochloric acid and nitric acid give?

Tin.

1. Stannous chloride and hydrogen sulfide give?
2. Stannous sulfide and ammonium polysulfide give?
3. Stannic chloride and hydrogen sulfide give?
4. Stannic sulfide and ammonium polysulfide give?
5. Ammonium thiostannate and hydrochloric acid give?
6. Stannic sulfide and hydrochloric acid give?
7. Stannic chloride and aluminium give tin and ?
8. Tin and concentrated hydrochloric acid give?
9. Stannous chloride and mercuric chloride (in excess) give?

Show by means of equations the action of sodium hydroxide, and of sodium carbonate, upon arsenious, antimonious, stannous, and stannic chlorides.

Ammonium polysulfide and hydrochloric acid give?

How may we determine whether the hydrogen sulfide precipitate (Group II) contains only sulfides of the copper group, only those of the tin group, or both?

Why is a long time sometimes required for the formation of the magnesium ammonium arsenate precipitate? How may its formation be hastened? Explain.

Explain the formation of antimony trichloride when antimony pentasulfide is dissolved in concentrated hydrochloric acid.

Name, and explain the nomenclature of the following compounds: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$.

Explain by means of the ionic theory and the law of mass action the fact that stannic sulfide dissolves readily in concentrated hydrochloric acid, but not in the diluted acid. If you had a strongly acid solution of stannic chloride, how would you quantitatively precipitate the tin?

In what three ways may the presence of an element be detected? (See the confirmatory tests for arsenic, antimony, and tin.)

Why may we not prepare hydrogen sulfide by the action of nitric acid upon ferrous sulfide?

GROUP III.

A. THE ALUMINIUM GROUP.

Aluminium.

1. Aluminium sulfate and ammonium hydroxide (in the presence of ammonium chloride) give?
2. Aluminium sulfate, ammonium sulfide and water give aluminium hydroxide, hydrogen sulfide and ?
3. Aluminium hydroxide and hydrochloric acid give?
4. Sodium peroxide and water give sodium hydroxide and ?
5. Aluminium hydroxide and sodium hydroxide give?
6. Sodium aluminate and nitric acid (in excess) give?
7. Aluminium nitrate and ammonium hydroxide give?
8. Aluminium hydroxide evaporated to dryness gives aluminium oxide and ?
9. Aluminium oxide (if not ignited) and hydrochloric acid give?
10. Silicic acid evaporated to dryness gives silicon dioxide and ?

Chromium.

1. Potassium chromate and dilute hydrochloric acid give?
2. Potassium dichromate, hydrochloric acid, and hydrogen sulfide give?
3. Chromium chloride and ammonium hydroxide give?
4. Chromium hydroxide and nitric acid give?
5. Chromium nitrate and sodium hydroxide give?
6. Chromium hydroxide and sodium peroxide give?
7. Sodium chromate and acetic acid give?
8. Sodium dichromate, barium chloride and ? give barium chromate and ?

An orange-colored solution, which turns green on passing hydrogen sulfide into it, then gives a greenish precipitate with ammonium hydroxide. The greenish precipitate dissolves in sodium peroxide; but on acidifying with acetic acid a bluish or violet colored liquid results, which gives no precipitate with lead acetate. On boiling, however, a copious yellow precipitate is obtained. Account for the phenomena.

Zinc.

1. Zinc chloride and ammonium sulfide give?
2. Zinc sulfide and hydrochloric acid give?
3. Zinc chloride and sodium hydroxide (not in excess) give?
4. Zinc hydroxide and sodium hydroxide (excess) give?
5. Sodium zincate and acetic acid give?
6. Zinc acetate and hydrogen sulfide give?
7. Sodium peroxide and acetic acid give?
8. Hydrogen peroxide and hydrogen sulfide give?

Show by means of equations the action of sodium carbonate solution upon aluminium, chromium, and zinc salt solutions.

If we dissolve a mixture of manganese and zinc sulfides in hydrochloric acid and wish to separate the metals by means of sodium hydroxide, why is it necessary to first boil off the hydrogen sulfide?

Explain by means of the ionic theory and the law of mass action the fact that zinc sulfide is readily soluble in dilute hydrochloric acid, but not in acetic acid. Is zinc sulfide soluble in a mixture of equal volumes of dilute hydrochloric acid and saturated sodium acetate solution? Explain.

Why is it necessary to add sodium carbonate solution in the separation of the aluminium and iron groups, unless the alkali earth metals are known to be absent? Explain.

Explain the fact that zinc hydroxide will dissolve in either hydrochloric acid or sodium hydroxide. What are such hydroxides called? Is lead hydroxide soluble in ammonia? Is zinc hydroxide? Explain their different behavior in this respect.

B. THE IRON GROUP.

Manganese.

1. Manganese nitrate and ammonium sulfide give?
2. Manganese sulfide and hydrochloric acid give?
3. Manganese chloride and sodium hydroxide give?
4. Manganese hydroxide, sodium peroxide, and water give hydrated manganese dioxide, $MnO(OH)_2$, and ?
5. Manganese dioxide and hydrochloric acid give?
6. Manganese dioxide, hydrogen peroxide, and nitric acid give?
7. Manganese nitrate, nitric acid, and potassium chlorate give?
8. Hydrated manganese dioxide, nitric acid, and lead peroxide give?

Iron.

1. Ferric chloride and hydrogen sulfide give?
2. Ferrous chloride and ammonium sulfide give?
3. Ferrous sulfide and hydrochloric acid give?
4. Ferrous chloride and sodium hydroxide give?
5. Ferrous hydroxide, sodium peroxide, and water give?
6. Ferric hydroxide and nitric acid give?
7. Ferric nitrate and potassium ferrocyanide give?
8. Ferric chloride and ammonium thiocyanate give?
9. Ferric chloride and ammonium acetate give?

10. Ferric acetate solution on boiling gives?
11. Ferrous sulfate and potassium ferrocyanide give?
12. Ferrous sulfate and potassium ferricyanide give?
13. Ferric chloride and potassium ferricyanide give?
14. Prussian blue and potassium hydroxide give?

Why is iron always in the ferrous condition when we get to the third group? Is ferrous iron precipitated by ammonium hydroxide in the presence of ammonium chloride and in the absence of air? (If you do not know, saturate a solution of ferric chloride with hydrogen sulfide, filter, boil to expel hydrogen sulfide, add an equal volume of concentrated ammonium chloride solution, made by dissolving the solid salt in freshly boiled water, and then at once add ammonium hydroxide.)

Cobalt.

1. Cobalt nitrate and ammonium sulfide give?
2. Cobalt sulfide and dilute hydrochloric acid give?

Account for the facts that cobalt and nickel sulfides are not precipitated by hydrogen sulfide from dilute hydrochloric acid solution, and yet they do not dissolve at all readily on treatment with dilute hydrochloric acid.

3. Cobalt sulfide and *aqua regia* give?
4. Cobalt chloride and sodium hydroxide give?
5. Cobaltous hydroxide, sodium peroxide and water give cobaltic hydroxide and ?
6. Cobaltic hydroxide and concentrated nitric acid upon boiling give cobaltous nitrate, oxygen and ?
7. Cobaltous nitrate and ammonium hydroxide give?
8. Cobaltous nitrate and ammonium thiocyanate give?

Nickel.

1. Nickel nitrate and ammonium sulfide give?
2. Nickel sulfide and *aqua regia* give?
3. Nickel chloride and sodium hydroxide (in the presence of sodium peroxide) give?

4. Nickel hydroxide and nitric acid give?
5. Nickel nitrate and ammonium hydroxide give?

What is the action of ammonium hydroxide on the salts of each metal of Group III, in the presence of ammonium salts? In the absence of ammonium salts?

Explain according to the ionic theory and the law of mass action why magnesium is not precipitated by ammonium hydroxide and ammonium carbonate in the presence of ammonium chloride.

Show by means of equations the action of sodium carbonate solution upon manganese, iron, cobalt, and nickel salts.

GROUP IV.

Barium.

1. Barium chloride and ammonium carbonate give?
2. Barium carbonate and acetic acid give?
3. Barium acetate and calcium sulfate give?
4. Barium acetate, water and potassium dichromate give?
5. Barium chromate, hydrochloric acid and alcohol give on boiling?
6. Barium chloride and sulfuric acid give?

Strontium.

1–3. As with barium.
4. Strontium acetate and potassium dichromate give?
5. Strontium acetate and ammonium carbonate give?
6. Strontium carbonate and acetic acid give?
7. Strontium acetate and calcium sulfate give?
8. Strontium acetate and ammonium sulfate give?

Calcium.

1–8. As with strontium.
9. Calcium sulfate and ammonium oxalate give?

What are the solubility relations of calcium, strontium, and barium salts?

GROUP V.

Magnesium.

1. Magnesium chloride, ammonium hydroxide and sodium phosphate in the presence of ammonium chloride give?

Sodium.

1. Flame color of sodium salts is?
2. Flame color of a mixture of sodium and potassium salts is?
3. Sodium chloride and hydrofluosilicic acid give?

Potassium.

1. Flame color of potassium salts is?
2. Potassium chloride and perchloric acid give?
3. Potassium chloride and hydrofluosilicic acid give?

Ammonium.

1. Flame color of ammonium salts is?
2. Ammonium chloride and sodium hydroxide upon warming give?
3. Ammonium hydroxide and hydrofluosilicic acid give ammonium fluoride, silicic acid and ?
4. Ammonium chloride and nitric acid are in equilibrium with ? and ?
5. Ammonium nitrate upon ignition gives?

QUESTIONS FOR REVIEW.

1. Outline the analysis of Group I, giving equations for the final tests.

2. A solution contains $CrCl_3$, $MnCl_2$, $FeCl_2$, and $NiCl_2$. How may the four metals be separated?

3. Write reactions for the preparation of the following substances: Prussian blue; ammonium thioarsenate; copper ferrocyanide; sodium stannite; ammonium sulfide.

4. Starting with a mixture of lead and chromium hydroxides, how may lead chromate be prepared? Write the reactions.

5. Outline the analysis of Group II, giving the reactions in the case of the final tests.

6. Tell exactly how arsenic and cadmium can be completely precipitated by H_2S, starting with a solution of cadmium arsenate in strong nitric acid.

7. What effect does sodium hydroxide solution have on each of the following ions? Which precipitates dissolve in an excess of the reagent, and what is formed in each case? Ag^+, Pb^{++}, Hg^{++}, Cd^{++}, Cu^{++}, Sn^{++}, Sn^{++++}, As^{+++}, Fe^{++}, Cr^{+++}, Al^{+++}, Mn^{++}, Zn^{++}, H^+.

8. Explain by means of the ionic theory and the law of mass action why zinc may be precipitated by H_2S from a hydrochloric acid solution, to which a large quantity of $NaC_2H_3O_2$ has been added.

9. Define oxidation. Reduction. Write equations for five reactions in which oxidation and reduction take place; underline the substances which are oxidized.

10. Name the group reagents and members of each group of metals. Write the formulas of the compounds precipitated in Group II by the group reagent, and give the color of each.

11. Outline the analysis of Group III, giving equations in the

case of the final tests. Give the colors of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, CoS, NiS, Mns, ZnS, FeS.

12. A solution contains a copper salt. Write equations showing the successive changes through which the copper passes in the course of an analysis.

13. Same for each of the other metals.

14. How may pure silver be obtained from coin silver (which contains 10 per cent. of copper)? Write the reactions.

15. Starting with barium sulfate, how may barium chloride be prepared? Write the reactions.

16. When an alkaline solution is acidified with HCl, what substances may be precipitated? How would you analyze such a solution?

17. If, in the course of an analysis, on adding ammonium sulfide to the solution, in order to precipitate Group III, you should obtain a flocculent yellow precipitate, what could it be? To what error may its presence here be due?

18. Outline the analysis of Groups IV and V. Name and give the formulas of the insoluble salts of ammonium and potassium.

19. Give a method for the detection of cadmium in a solution which also contains copper, and explain it. Write the reactions that take place.

20. What error may cause the filtrate from the ammonium sulfide precipitate (Group III) to be dark in color? What is the procedure if this is the case?

21. Why is it necessary to add $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ to the filtrate from Group IV before testing for the metals of Group V?

22. Explain by means of the ionic theory and the law of mass action why the presence of ammonium chloride prevents the precipitation of magnesium by NH_4OH.

23. What is the effect of the presence of phosphates on the precipitation of Group III? Explain your answer.

24. A solution contains $CdCl_2$, $ZnCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_2$, and $BaCl_2$. How may the six metals be separated? Write the reactions.

25. A solution containing the six salts mentioned in the preceding question also contains phosphoric acid. How may the six metals be separated?

26. In the separation of the aluminium and iron groups, why is it necessary to add Na_2CO_3 solution unless the alkali earth metals are known to be absent? Explain.

27. Arrange the sulfates of the metals of Group IV in the order of their solubility. Also the oxalates and the chromates.

28. How may chromates be converted into dichromates; dichromates into chromates; dichromates into chromium salts; chromium salts into chromates? Illustrate each with an equation. Give the characteristic colors of chromates, dichromates, and chromium salts.

29. Name the members of each group of acids, and tell how the presence of each group may be detected.

30. Complete the following equations:

$$CrCl_3 + Na_2CO_3 + H_2O \rightarrow$$
$$AlCl_3 + Na_2CO_3 + H_2O \rightarrow$$
$$AlCl_3 + (NH_4)_2S + H_2O \rightarrow$$

Explain in terms of the ionic theory how these reactions take place. Why does a solution of Na_2CO_3 in water react alkaline? Why does a solution of $FeCl_3$ in water react acid?

31. Explain in terms of the ionic theory the precipitation of $SrSO_4$ by $CaSO_4$ solution, and the absence of precipitation when the latter is added to a dilute solution of a soluble salt of calcium.

32. What are the tests for sulfuric, sulfurous, thiosulfuric, and hydrobromic acids? Write the reactions, starting with sodium salts.

33. How may the following transformations be effected? (Write the reactions.) Potassium ferrocyanide to potassium ferricyanide. Sodium sulfite to sodium sulfate. Nitrous acid to nitric acid. Nickelous hydroxide to nickelic hydroxide. Silica to hydrofluosilicic acid.

34. What salts, if any, of the following acids are insoluble: sulfuric, hydrochloric, acetic, nitric, and carbonic?

35. Describe the brown-ring test for nitric acid. Write the reactions, starting with $NaNO_3$.

36. How may phosphoric and arsenic acids be detected in the same solution?

37. How may chlorides, bromides, and iodides be detected in the same solution? Write the reactions, starting with sodium salts.

38. How may oxalic and carbonic acids be detected in the same unknown? Write the reactions, using calcium salts.

39. What acids form barium salts which are insoluble in water? What happens when $AgNO_3$ solution is added in excess to a cold solution of $Na_2S_2O_3$? Explain.

40. What inference do you draw from the fact that the chromates of calcium and strontium are not precipitated in presence of acetic acid, while $BaCrO_4$ is so precipitated? Explain in terms of the ionic theory the non-precipitation of $BaCrO_4$ in the presence of hydrochloric acid.

41. What indications may be derived from the preliminary test with conc. H_2SO_4 in regard to the acids present in an unknown substance?

42. Can As be precipitated from solution with Na_2CO_3? Why? Do any other members of the first four groups of metals (including Mg) resemble arsenic in this respect? What use is made of this fact in qualitative analysis? May Mg be precipitated from a solution containing NH_4Cl by boiling with Na_2CO_3? Explain your answer.

43. Explain the non-precipitation of Cd^{++} by H_2S if the solution is strongly acid with HCl. Would the result be different if much $NaC_2H_3O_2$ were added to the strongly acid solution? Explain. Why then do we not add $NaC_2H_3O_2$ solution in the precipitation of Group II?

44. How may the presence of nitrate be detected in a substance known to contain chlorate? What is the purpose of the Na_2CO_3 used in this test?

45. Give tests for hydrofluoric, silicic, nitrous, and acetic acids.

46. How may we determine whether the H_2S precipitate (Group II) contains only sulfides of the copper group, only those of the tin group, or both? If both are present, how may we know when we have completely separated them?

47. What ions are furnished by the salt $KFe(SO_4)_2.12H_2O$, when it is dissolved in water? By $(NH_4)_2Fe(SO_4)_2.6H_2O$? What is the class-name of such salts? How do they differ from salts like $Ag(NH_3)_2Cl$, $KAg(CN)_2$, $K_4Fe(CN)_6$, etc.? What is the class-name of these salts? Is there any sharp dividing line between these two classes of salts? Illustrate.

48. Upon warming Hg_2SO_4 with HCl, a gas with a suffocating odor is evolved; why? Copper sulfite, a brick-red powder of the formula $CuSO_3$, is soluble in dilute HCl, but a white precipitate of Cu_2Cl_2 soon separates from the solution; account for this.

49. In testing a substance known to contain mercury for acetic acid with conc. H_2SO_4 and alcohol, a disagreeable, suffocating odor was obtained, instead of the pleasant odor of ethyl acetate. Upon adding conc. H_2SO_4 to a little of the moistened substance in a watch glass, however, the odor of acetic acid was very distinct. Account for the failure of the first test.

50. Explain why silver sulfide (which is less soluble in water than the chloride) is soluble in nitric acid, while the chloride is not.

PREPARATION OF REAGENTS.

Acetic acid: Sp. gr. 1.041 (30 per cent. $HC_2H_3O_2$); mix 1 liter of glacial acetic acid with 2.5 liters of water.

Ammonium acetate: Add 1000 cc. NH_4OH (sp. gr. 0.90) to 900 cc. glacial acetic acid and neutralize the mixture with more NH_4OH or $HC_2H_3O_2$. For a 50 per cent. solution, dilute to sp. gr. 1.092; for a 10 per cent. solution, dilute to sp. gr. 1.022.

Ammonium carbonate:
250 grams "am. carbonate"
100 cc. NH_4OH (sp. gr. 0.90)
1000 cc. water.
Digest in a closed bottle.

Ammonium chloride: 1:10.

Ammonium hydroxide: Sp. gr. 0.96 (10 per cent. NH_3).
1 liter NH_4OH (sp. gr. 0.90)
2 liters water.

Ammonium molybdate: Mix 100 grams MoO_3 with 400 cc. cold water and add 80 cc. NH_4OH (sp. gr. 0.90). Filter, and pour the filtrate with constant stirring into a mixture of 300 cc. HNO_3 (sp. gr. 1.42) and 700 cc. water.

Ammonium oxalate: 1:25. Use warm water.

Ammonium polysulfide: Pass the gas evolved from the action of 200 cc. conc. commercial H_2SO_4, properly diluted, upon an excess of FeS (calculated about 360 grams), into 1 liter NH_4OH (sp. gr. 0.96). Dissolve 25 grams of flowers of sulfur in each liter of solution.

Ammonium sulfate: 1:4.

Ammonium thiocyanate: 1:10.

Barium chloride: 1:40.

Barium hydroxide: 1:20.

Bromine water: Saturated solution.

Calcium chloride: 1:10.

Calcium hydroxide: Saturated (filtered) solution.

Calcium sulfate: Saturated (filtered) solution.

Chlorine water: Saturated solution. Keep in opaque glass-stoppered bottles.

Chloroplatinic acid: 1:50.

Cobalt nitrate: (1 cc. contains 0.5 mg. metallic cobalt); 2.5 grams $Co(NO_3)_2.6H_2O$ in 1 liter.

Ferric chloride: 1:10.

Ferric sulphate: Take 200 grams $FeSO_4.7H_2O$, add 200 cc. dil. H_2SO_4 and 12 cc. conc. HNO_3. Heat rapidly to boiling and boil vigorously for some time to expel the nitric oxide. Dilute to 1 liter.

Ferrous sulphate:

400 grams $FeSO_4.7H_2O$.
200 grams $(NH_4)_2SO_4$.
100 cc. conc. H_2SO_4.
1000 cc. water.

The solution will keep well enough to use in tests for HNO_3 for several months. It should not be used in the test for hydrocyanic acid.

Hydrochloric acid (conc.): Sp. gr. 1.19 (37 per cent. HCl).

Hydrochloric acid (dil.): Sp. gr. 1.12 (24 per cent. HCl); mix 1 liter HCl (sp. gr. 1.19) with 700 cc. water.

Hydrogen peroxide: 3 per cent. solution.

Lead acetate: 1:10.

Magnesia mixture: Dissolve 90 grams $MgCl_2.6H_2O$ and 240 grams NH_4Cl in 1 liter of water, and add 50 cc. NH_4OH (sp. gr. 0.90).

Mercuric chloride: 1:20.

Nitric acid (conc.): Sp. gr. 1.42 (70 per cent. HNO_3).

Nitric acid (dil.): Sp. gr. 1.20 (32 per cent. HNO_3); mix 1 liter HNO_3 (sp. gr. 1.42) with 1675 cc. water.

Nessler's Solution: Dissolve 6 grams $HgCl_2$ in 50 cc. ammonia-free water at 80° in a porcelain dish, add a solution of 7.4 grams KI in 50 cc. ammonia-free water, cool, decant the liquid, and wash the precipitate by decantation with three separate 20 cc.

portions of cold water. Now add 5 grams solid KI, and enough water to dissolve the mixture, transfer the solution to a 100 cc. measuring flask, add a solution of 20 grams NaOH in a little water, cool, and dilute the volume to 100 cc. Allow the mixture to settle, siphon off the colorless liquid into a clean bottle and preserve it in the dark.

Perchloric acid: Sp. gr. 1.12 (20 per cent. $HClO_4$).

Potassium cyanide: 1:10.

Potassium dichromate: 1:10. Use hot water.

Potassium ferrocyanide: 30 grams $K_4Fe(CN)_6.3H_2O$ in 1 liter.

Potassium nitrite: 3:10.

Potassium thiocyanate: 1:10.

Silver nitrate: 1:40.

Silver sulfate: Saturated solution.

Sodium acetate: Saturated solution.

Sodium carbonate: 100 grams of anhydrous salt in 1 liter.

Sodium hydroxide; 1:10.

Sodium phosphate: 1:10.

Sulfuric acid (conc.): Sp. gr., 1.84 (96 per cent. H_2SO_4).

Sulfuric acid (dil.): Sp. gr. 1.19 (26 per cent. H_2SO_4); mix 1 volume of conc. H_2SO_4 (sp. gr. 1.84) with 5 volumes of cold water, slowly adding the acid to the water with constant stirring.

Stannous chloride: Dissolve 125 grams $SnCl_2.2H_2O$ in 1 liter of water, with the addition of conc. HCl, and keep the solution in bottles containing granulated tin.

TABLE OF

	Arsenate.	Arsenite.	Chromate.	Sulfate.	Phosphate.	Borate.	Oxalate.	Fluoride.	Carbonate.	Silicate.	Chloride.
Silver........	HNO_3	HNO_3	HNO_3	W-A	HNO_3	HNO_3	HNO_3	W	HNO_3	......	I
Mercury (ous)...	HNO_3	HNO_3	HNO_3	W-A	HNO_3	......	HNO_3	HNO_3	HNO_3	......	HNO_3
Mercury (ic).....	HCl	HCl	W-A	W-A	HCl	......	HCl	HNO_3	HCl	......	W
Lead...........	HNO_3	HNO_3	A-I	A-I	HNO_3	HNO_3	HNO_3	HNO_3	HNO_3	HNO_3	W-A
Bismuth.........	HCl	......	HCl	W-A	HCl	HCl	HCl	HNO_3	HCl	......	W-A
Copper..........	HCl	HCl	W	W	HCl	HCl	HCl	HCl	HCl	HCl	W
Cadmium........	HCl	......	HCl	W	HCl	W-A	HCl	W-A	HCl	HCl	W
Tin (ous)........	HCl	HCl	HCl	W	HCl	HCl	HCl	W	......	......	W
Tin (ic)..........	HCl	......	......	......	HCl	......	W	W	......	......	W
Antimony........	HCl	HCl	HCl	HCl	W-A	......	HCl	W	......	......	W-A
Iron (ous)........	HCl	HCl	......	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Iron (ic).........	HCl	HCl	W	W	HCl	HCl	HCl	A-I	HCl	HCl	W
Aluminium......	HCl	......	......	W	HCl	HCl	HCl	A-I	......	A-I	W
Chromium	HCl	......	HCl	W or I	HCl	HCl	W-A	A-I	......	HCl	W or I
Cobalt..........	HCl	HCl	HCl	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Nickel..........	HCl	HCl	HCl	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Manganese......	HCl	HCl	W	W	HCl	HCl	W-A	W-A	HCl	HCl	W
Zinc...........	......	......	W	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Barium.........	HCl	HCl	HCl	I	W&A	HCl	HCl	A-I	HCl	HCl	W
Strontium.......	HCl	HCl	W-A	I	W&A	HCl	HCl	A-I	HCl	HCl	W
Calcium........	HCl	HCl	W-A	W-I	W&A	HCl	HCl	A-I	HCl	HCl	W
Magnesium.....	HCl	HCl	W	W	HCl	W-A	HCl	A-I	HCl	HCl	W
Potassium......	W	W	W	W	W	W	W	W	W	W	W
Sodium........	W	W	W	W	W	W	W	W	W	W	W
Ammonium.....	W	W	W	W	W	W	W	W	W	......	W

HNO_3. Soluble in HNO_3, in most cases insoluble, or slightly soluble in HCl
HCl. Soluble in HCl, in many cases soluble in other acids, also.
W. Soluble in water.

SOLUBILITIES.

Bromide.	Iodide.	Cyanide.	Ferro-cyanide.	Ferri-cyanide.	Sulfide.	Nitrate.	Chlorate.	Acetate.	Tartrate.	Citrate.	Oxide.	Hydroxide.	
I	I	I	I	I	HNO_3	W	W	W	HNO_3	HNO_3	HNO_3	......	Silver.
HNO_3	HNO_3	......	......	......	AqReg	W	W	W-A	W-A	HNO_3	HNO_3	......	Mercury (ous)
W	HNO_3	W	......	......	AqReg	W	W	W	HCl	W-A	HCl	......	Mercury (ic).
W-A	W-A	HNO_3	A	W-A	HNO_3	W	W	HNO_3	HNO_3	HNO_3	HNO_3	HNO_3	Lead.
W-A	HCl	......	......	......	HNO_3	W-A	W	W	HCl	......	HCl	HCl	Bismuth.
W	W	HCl	I	......	HNO_3	W	W	W	W	W	HCl	HCl	Copper.
W	W	HCl	......	......	HNO_3	W	W	W	W-A	HCl	HCl	HCl	Cadmium.
......	W	......	......	......	HCl	....	W	W	HCl	......	HCl	HCl	Tin (ous).
......	W	......	......	......	HCl	....	..	W	......	......	A&I	HCl	Tin (ic).
W-A	W-A	......	......	......	HCl	....	..	......	W-A	......	HCl	HCl	Antimony.
W	W	A-I	I	I	HCl	W	W	W	W-A	W	HCl	HCl	Iron (ous).
W	W	......	I	W	AqReg	W	W	W	W	W	HCl	HCl	Iron (ic).
W	W	......	......	......	HCl	W	W	W	W	W	A&I	HCl	Aluminium.
W or I	W	HCl	......	......	A-I	W	W	W	W	W	A&I	HCl	Chromium.
W	W	A-I	I	I	HNO_3	W	W	W	W	W	HCl	HCl	Cobalt.
W	W	A-I	I	I	HNO_3	W	W	W	HCl	W	HCl	HCl	Nickel.
W	W	HCl	HCl	I	HCl	W	W	W	W-A	HCl	HCl	HCl	Manganese.
W	W	HCl	A-I	HCl	HNO_3	W	W	W	HCl	W-A	HCl	HCl	Zinc.
W	W	W-A	W-A	......	W	W	W	W	HCl	HCl	W	W	Barium.
W	W	W	W	......	W	W	W	W	HCl	HCl	W	W	Strontium.
W	W	W	W	W	W-A	W	W	W	HCl	W-A	W-A	W-A	Calcium.
W	W	W	W	W	HCl	W	W	W	W-A	W	HCl	HCl	Magnesium.
W	W	W	W	W	W	W	W	W	W	W	W	W	Potassium.
W	W	W	W	W	W	W	W	W	W	W	W	W	Sodium.
W	W	W	W	W	W	W	W	W	W	W	......	W	Ammonium.

W-A. Slightly soluble in water, soluble in acids.
A-I. Insoluble in water, slightly soluble in acids.
I. Insoluble in water and acids.